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DEFINITIVE DETERMINATIONS OF THE SOLUBILITIES OF OXYGEN AND HYD--ETC(U)
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FINAL TECHNICAL REPORT

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Office of Naval Research

Definitive Determinations of the Solubilities
of Oxygen and Hydrogen, and Verification of
the Applicability of the Setschenow
Relationship to Sea Water.

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18 November 1980

Amherst College, Amherst, Mass. 01002

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Dr. Daniel Krause, Jr., Co-Principal Investigator

Letter on file



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This final technical report is composed of two reprints (attached) plus the following summary of those two papers and a discussion of other work that is now in preparation for publication.

1. Oxygen: It was noted in the original proposal (p. 6) that "we make corrections to the fugacity for gas-gas and gas-water interactions in the vapor phase." Corrections for molecular interactions in a pure gas can be made from a knowledge of the virial coefficients for the gas. The presence of water vapor, however, complicates the problem, especially at higher temperatures, where the vapor pressure of water becomes larger. In the absence of experimental knowledge about gas-water interactions, we were using theoretical calculations to estimate the effect of the interaction. After it was found that the theoretical methods did not provide corrections to the solubility data with sufficient accuracy, we finally decided to adopt the direct empirical approach described in the attached reprint from Vol. 8, No. 9 (Benson, Krause and Peterson, 1979) of the Journal of Solution Chemistry. Although additional time is required to carry out the measurements from which the effect of the total pressure is determined, the results for the Henry coefficient are unequivocal and fully corrected.

The precision of the measurements of the solubility of oxygen (random error less than 0.02%) is an order of magnitude better than previous measurements on any gas over a significant

temperature range, and tests and comparison with other work indicate that systematic errors probably are negligible. Furthermore the accuracy of the measurements has made it possible to show that the expression

$$\ln k = a_0 + a_1/T + a_2/T^2$$

is a much better way to express the variation of solubility with temperature than the relationships previously used. Mass spectrometric measurements of the isotopic fractionation of $^{34}\text{O}_2/^{32}\text{O}_2$ during solution have provided the first quantitative determination of the variation of the fractionation with temperature, and have made possible an estimation of the size of the cavity occupied by the oxygen molecule in the water.

A second manuscript, "The concentration and isotopic fractionation of gases dissolved in freshwater in equilibrium with the atmosphere: 1. Oxygen," has been published in "Limnology and Oceanography" (Benson and Krause, 1980). A copy is included here. In it we have discussed how to obtain accurate values for the concentration of an atmospheric gas in water in equilibrium with air, including corrections for molecular interactions in the vapor phase. The results for oxygen show that the UNESCO tables for the solubility of oxygen give values in freshwater that are low by from 0.15% to 0.35% depending upon temperature.

2. Hydrogen: We have carried out several sets of determinations of the solubility of hydrogen. The results give very accurate values for oceanographic and limnological work, and they are especially significant because of the information they provide about the properties of liquid water.

A) Pure Water: Fig. 1 shows the results of our measurements on hydrogen in distilled water from 0 to 60°C. The clusters of solid circles at 0, 15, 35 and 55°C are drawn to indicate that measurements at several pressures were made, from which the corrections for molecular interactions in the vapor phase were obtained. (All points really lie essentially on the line at the same temperature.) Although the virial coefficients for pure hydrogen show that it is a "repulsive gas," the hydrogen-water vapor system behaves very nearly like an ideal gas. In fact, the variation of λ with t (°C) is given by

$$\lambda = 0.000345 - 1.83 \times 10^{-5}t,$$

which shows that below approximately room temperature it is a slightly "attractive gas," but it becomes "repulsive" above room temperature. Comparison with Eq. 21 in Benson, Krause and Peterson (1979) shows that relative to oxygen the vapor phase correction is smaller and varies less rapidly with temperature. Again, our function

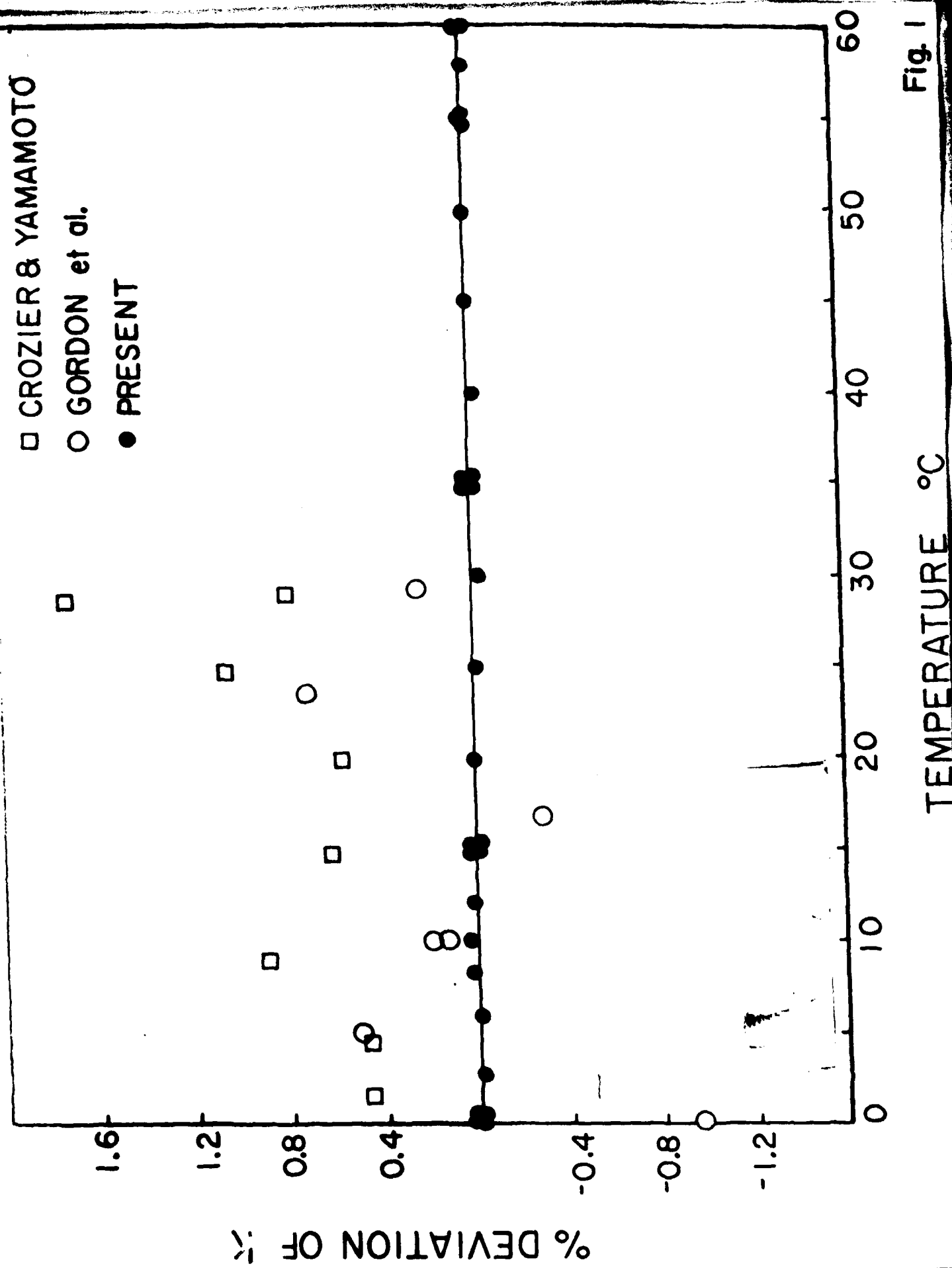


Fig. 1

$$\ln k = a_0 + a_1/T + a_2/T^2$$

provides an excellent fit for the data. The standard deviation for all the pure water measurements from 0 to 60°C is 0.016%. Fig. 1 also shows the experimental results of Crozier and Yamamoto (1974) and Gordon et al. (1977). The large scatter of their data is evident, together with systematic deviations from our results. Note that the ordinate axis has been compressed by a factor of two compared to Fig. 4 in BKP for oxygen, in order to keep the hydrogen points on the graph. It is possible to calculate the thermodynamic function changes for the solution of hydrogen in water, as we have done for oxygen, but these will not be discussed here.

- B) Seawater: Although it is well known that gas solubilities decrease with increasing salinity (the "salting-out" effect), the functional dependence of solubility on S has been difficult to determine because very accurate measurements are required. Carpenter (1966) found a non-linear variation for the solubility of O₂ with chlorinity, and he used a quadratic relationship. Green and Carritt (1967) reported a series of measurements on oxygen to obtain the ratio of the solubility in seawater to that in pure water. The design of the experiment made potential systematic errors in the individual solubility determinations tend to cancel in the ratio. Green and Carritt showed that

within the limits of their measurements the Setschenow relationship correctly describes the dependence of the oxygen ratio on chlorinity. Furthermore, their results provided the first reasonably accurate determination of the way the salting-out coefficient varies with temperature.

We have measured the dependence of solubility on salinity up to approximately 50‰ at 0, 10, 20 and 35°C. The results are shown in Fig. 2 where it is clear that $\ln (k_s/k_o)$ is extremely linear with salinity. (Fits to salinity and chlorinity are equally good.) Although the straight lines in Fig. 2 suggest that the Setschenow equation fits the results very well, the tightness of fit does not really become apparent until it is recognized that the precision of the measurements is such that even the slopes of the four lines are known with great accuracy (0°C: 0.46%, 10°C: 0.12%, 20°C: 0.15%, 35°C: 0.04%). In other words, these very accurate new results for hydrogen not only verify the applicability of the Setschenow relationship to hydrogen in seawater, but also now make it possible to determine the functional dependence of the salting-out coefficient upon temperature. This is illustrated in Fig. 3 where the salting-out coefficient is plotted vs. $1/T$. (Error bars are shown on the solid circle at 0°C, but the errors for the other three points are less than the size of the circles.) It is clear that

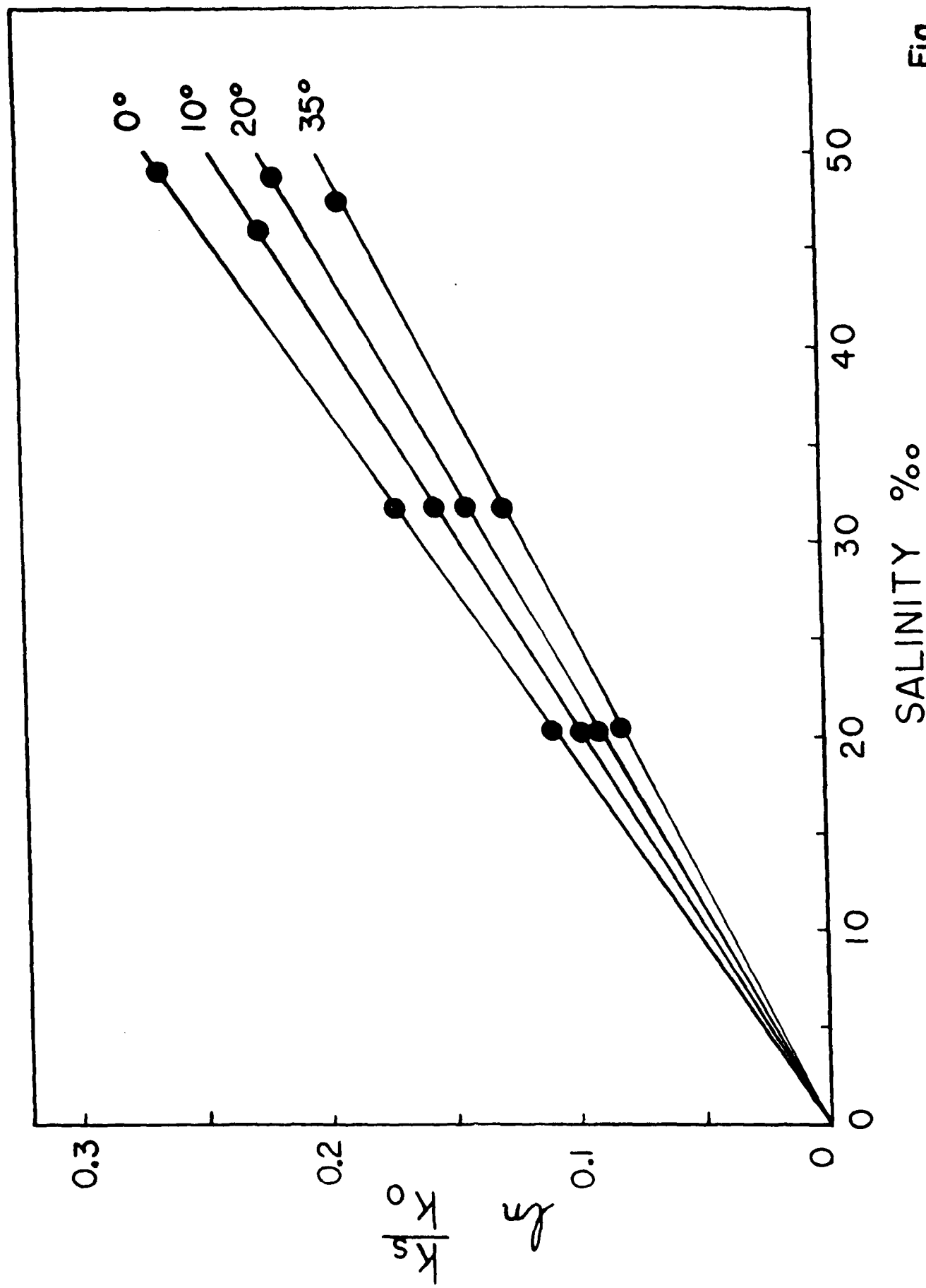


Fig. 2

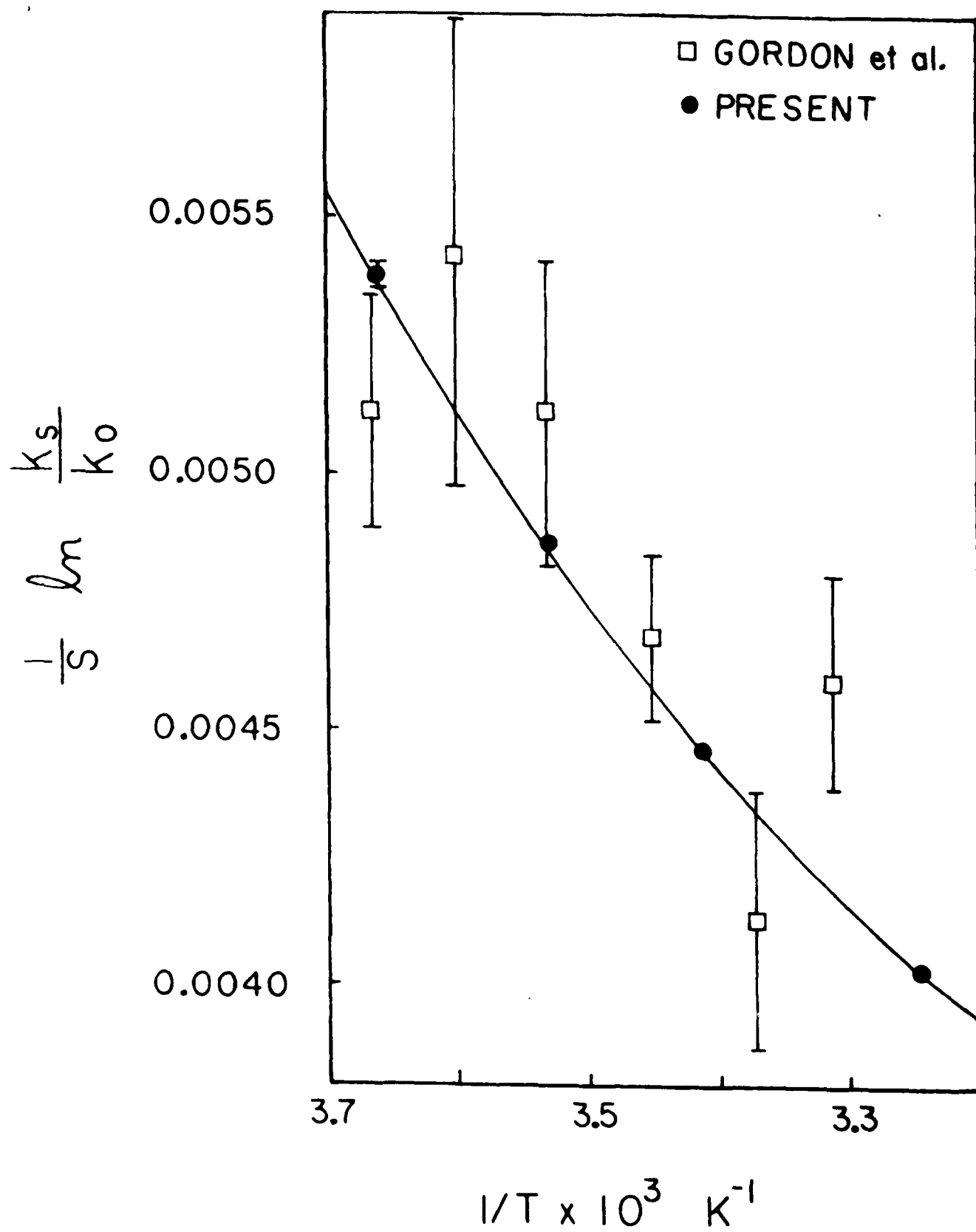


Fig. 3

the points lie on a smooth curve, and - like $\ln k$ - it is parabolic in $1/T$. The open squares representing the results of Gordon et al. are generally consistent with our values, although, of course, their much larger errors and scatter preclude determination of the temperature dependence with any certainty.

Our final equation for the variation of the Henry coefficient with both temperature and salinity is

$$\ln k = 4.13352 + 4672.47/T - 768235/T^2 + S(0.026112 - 15.684/T + 2737.0/T^2).$$

The salting-out coefficient in the parenthesis has its minimum at a temperature not very different from that for the solubility in pure water. The equation used by Green and Carritt for the Bunsen coefficient of oxygen was of the form

$$\ln \beta = A + B/T + C \ln T + DT + C_2(A' + B'/T + C' \ln T + D'T).$$

Gordon et al. fitted their hydrogen data together with those of Crozier and Yamamoto, to the following function

$$\ln \beta = A + B/T + C \ln T + S(A' + B'/T + C'T^2).$$

The fit of all our data (for both pure water and seawater) to our function is shown in Fig. 4. There were, of course,

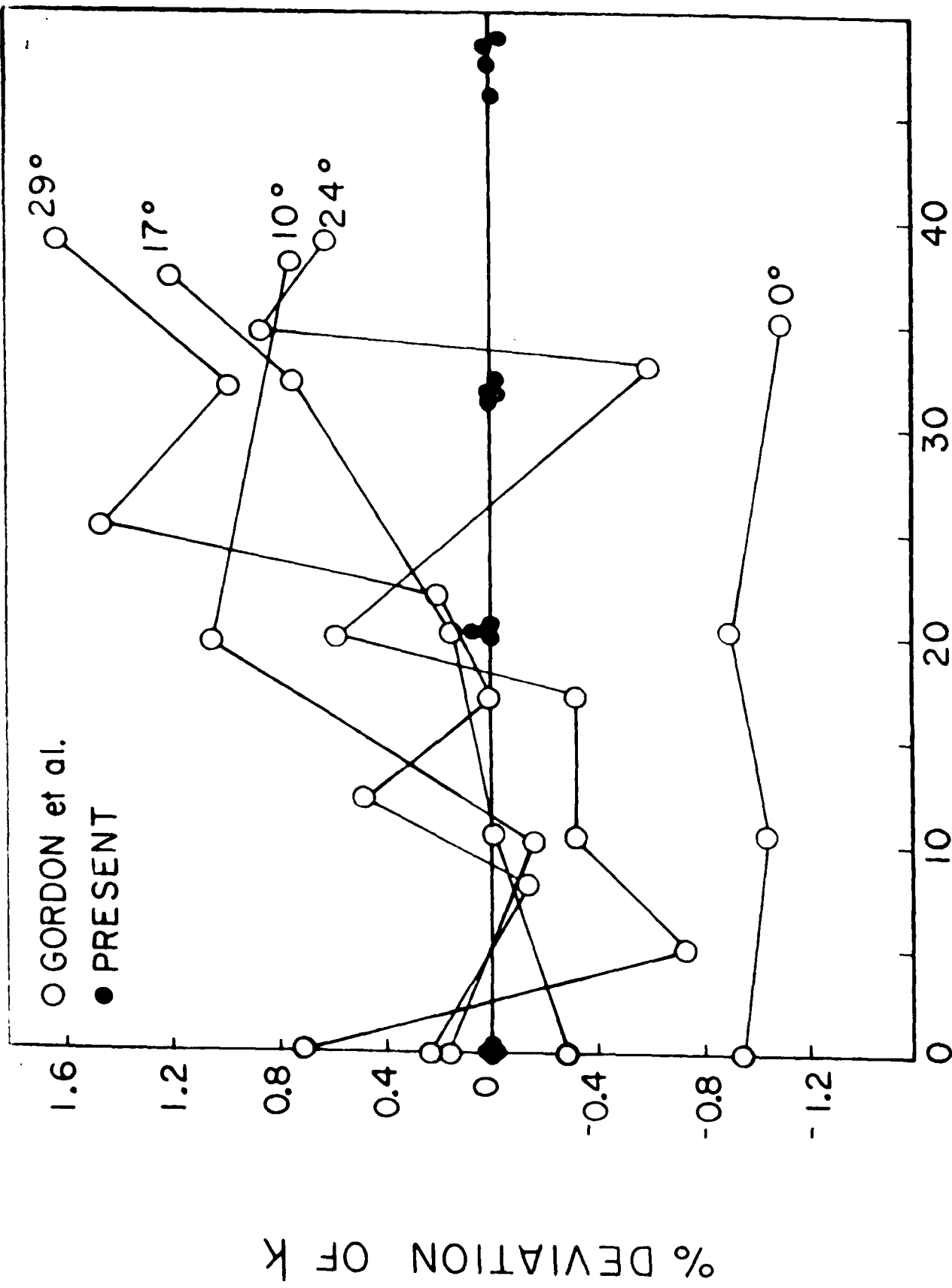


Fig. 4

SALINITY ‰

many more points at zero salinity than those indicated. The values of Gordon et al. also are shown as a function of salinity at five temperatures from 0 to 29°C. In addition to large fluctuations they exhibit apparent systematic deviations which depend upon temperature. Fig. 5 compares the experimental values of both Gordon et al. and Crozier and Yamamoto with our results for the temperature variation of the solubility of hydrogen in water with the 30-40% salinity range typical of the oceans.

3. Data accumulation and analysis system.

For very precise isotopic ratio measurements with the mass spectrometer we have designed and constructed a very convenient new system for taking and analyzing the data. It incorporates a voltage-to-frequency converter and commercially available timer, counter, and printer units into an automatic sample changing system that electronically averages noise from the difference amplifier in the null balance system. The system yields superb results. The precision achieved with electronic averaging of the noise is both greater and more objective than with visual averaging. In addition, the time for taking and analyzing the data is reduced by approximately 30%.

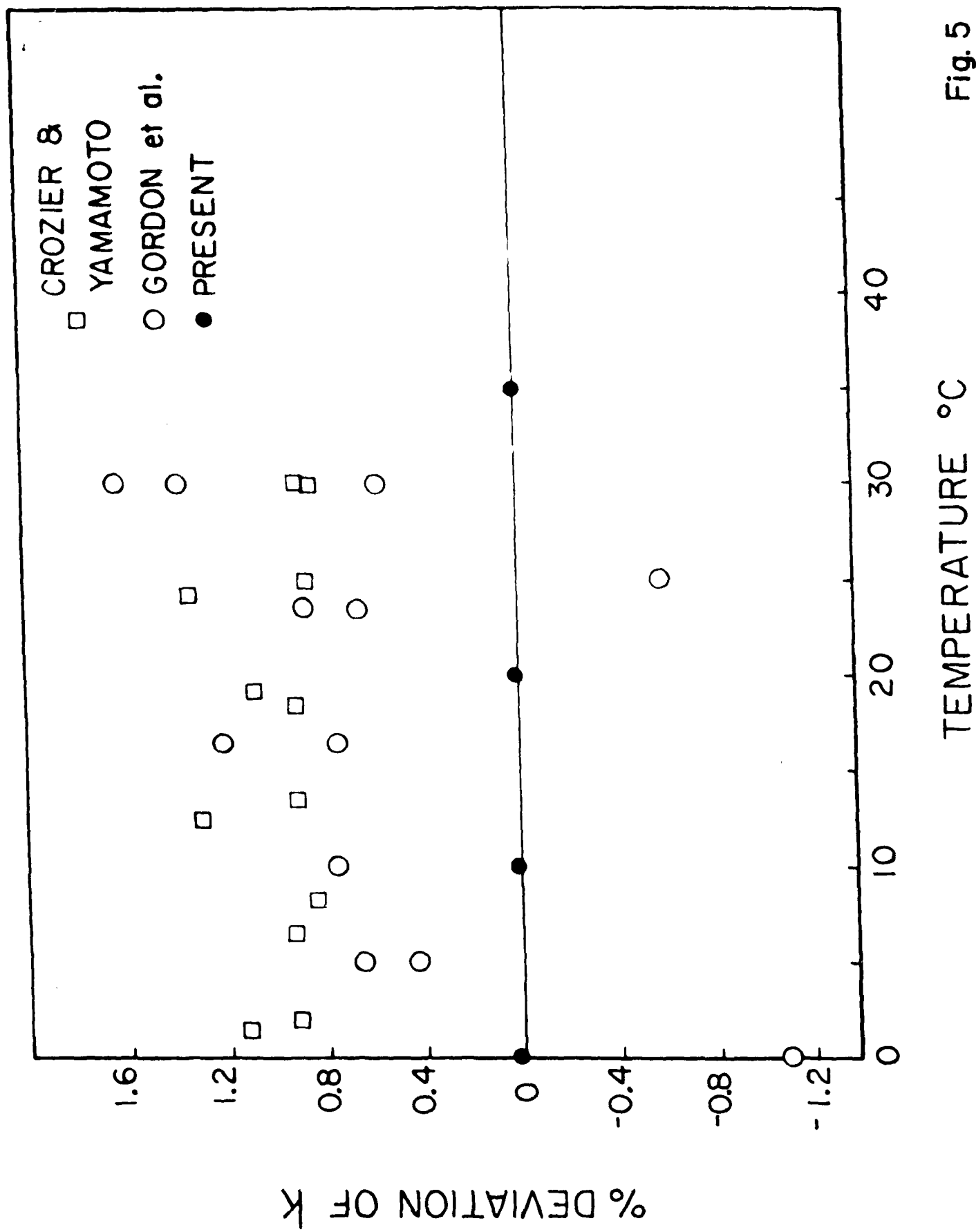


Fig. 5

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Journal of Solution Chemistry, Vol. 8, No. 9, 1979

**The Solubility and Isotopic Fractionation
of Gases in Dilute Aqueous Solution.
I. Oxygen**

**Bruce B. Benson, Daniel Krause, Jr.,
and Mark A. Peterson**

The Solubility and Isotopic Fractionation of Gases in Dilute Aqueous Solution.

I. Oxygen

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A very precise and accurate new method is described for determination of the Henry coefficient k and the isotopic fractionation of gases dissolved in liquids. It yields fully corrected values for k at essentially infinite dilution. For oxygen the random error for k is less than 0.02%, which is an order of magnitude better than the best previous measurements on that or any other gas. Extensive tests and comparison with other work indicate that systematic errors probably are negligible and that the accuracy is determined by the precision of the measurements. In the virial correction factor $(1 + \lambda P_i)$, where P_i is the total pressure of the vapor phase, the coefficient λ for oxygen empirically is a linear decreasing function of the temperature over the range 0–60°C. The simple three-term power series in $1/T$ proposed by Benson and Krause,

$$\ln k = a_0 + a_1/T + a_2/T^2$$

provides a much better form for the variation of k with temperature than any previous expression. With $a_0 = 3.71814$, $a_1 = 5596.17$, and $a_2 = -1049668$, the precision of fit to it of 37 data points for oxygen from 0–60°C is 0.018% (one standard deviation). The three-term series in $1/T$ also yields the best fit for the most accurate data on equilibrium constants for other types of systems, which suggests that the function may have broader applications. The oxygen results support the idea that when the function is rewritten as

$$\ln k = -(A_1 + A_2) + A_1\left(\frac{T_1}{T}\right) + A_2\left(\frac{T_1}{T}\right)^2$$

it becomes a universal solubility equation in the sense that A_2 is common to all gases, with T_1 and A_1 characteristic of the specific gas. Accurate values are presented for the partial molal thermodynamic function changes for the solution of oxygen in water between the usual standard states for the liquid and vapor phases. These include the change in heat capacity, which varies inversely with the square of the absolute temperature and for which the random error is 0.15%. Analysis of the high-temperature data of Stephan et al., in combination with our values from 0–60°C, shows that for oxygen the four-term series in $1/T$,

$$\ln k = -4.1741 + 1.3104 \times 10^4/T - 3.4170 \times 10^6/T^2 + 2.4749 \times 10^8/T^3$$

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where $p = kx$ and p is the partial pressure in atmospheres of the gas, probably provides the best and easiest way presently available to calculate values for k in the range 100–288°C, but more precise measurements at elevated temperatures are needed. The new method permits direct mass spectrometric comparison of the isotopic ratio $^{34}\text{O}_2/^{32}\text{O}_2$ in the dissolved gas to that in the gas above the solution. The fractionation factor $\alpha = ^{32}k/^{34}k$ varies from approximately 1.00085 (± 0.00002) at 0°C to 1.00055 (± 0.00002) at 60°C. Although the results provide the first quantitative determination of α vs. temperature for oxygen, it is not possible from these data to choose among several functions for the variation of $\ln \alpha$ with temperature. If the isotopic fractionation is assumed to be due to a difference in the zero-point energy of the two species of oxygen molecules, the size of the solvent cage is calculated to be approximately 2.5 Å. The isotopic measurements indicate that substitution of a $^{34}\text{O}_2$ molecule for a $^{32}\text{O}_2$ molecule in solution involves a change in enthalpy with a relatively small change in entropy.

KEY WORDS: Gas solubility; isotopic fractionation; oxygen; water; temperature dependence; Henry coefficient; thermodynamic functions.

1. INTRODUCTION

Although the solution of gases in water has been studied for approximately two centuries, obtaining accurate values for gas solubilities has proved to be difficult. The history of the subject has been reviewed thoroughly by Markham and Kobe,⁽¹⁾ Battino and Clever,⁽²⁾ Wilhelm, Battino, and Wilcock,⁽³⁾ and Franks.⁽⁴⁾ In this paper the discussion of earlier work on oxygen will be brief, except for a comparison of the results presented here with the best previous values.

Because a knowledge of its solubility is important for many kinds of work, oxygen has been studied more extensively and carefully than any other gas. In retrospect, the early measurements by Winkler^(5,6) and Fox⁽⁷⁾ during the last two decades of the 19th century and the first decade of the 20th must be considered very good for that period. They survived as standard values in the *Handbook of Chemistry and Physics*⁽⁸⁾ (Winkler), as standards for oceanographic work (Fox), and as standards for sanitation engineering (the oxygen values of Fox recalculated by Whipple and Whipple⁽⁹⁾) for a half century and longer. The accuracy of the Fox and Winkler values was brought into question in 1955 by the oxygen determinations of Truesdale, Downing, and Lowden,⁽¹⁰⁾ Morrison and Billett,⁽¹¹⁾ Steen,⁽¹²⁾ Morris, Stumm, and Galal,⁽¹³⁾ and Elmore and Hayes⁽¹⁴⁾ carried out new analyses on oxygen, and in 1961 Benson and Parker⁽¹⁵⁾ used mass spectrometric measurements of the solubility ratios N_2/Ar and N_2/O_2 to interrelate and evaluate existing data. The differences among workers indicated that the uncertainties in the solubility values were approximately 1–2%.

The need for better solubility values, primarily for the study of oxygen dissolved in natural waters, generated a series of attempts^(16–22) to achieve

higher accuracy. By 1970, as we shall see later, four laboratories, using different methods of equilibration and both gasometric and Winkler analytical techniques, had obtained agreement over the range 0–35°C within the scatter of their data, i.e., approximately $\pm 0.2\%$. Together, these constitute the most accurate solubility data currently available for any gas.

Various methods have been used to express solubility values as a function of temperature. Most recently, Wilhelm, Battino, and Wilcock,⁽³⁾ following Clarke and Glew,⁽²³⁾ have fitted a selected group of data for oxygen (and other gases) to a four-term series of the form

$$\ln k = a_0 + a_1/T + a_2 \ln T + a_3 T + \dots \quad (1)$$

where k is the Henry coefficient. This series is essentially an extension of the three-term function first derived by Valentiner.⁽²⁴⁾ Weiss⁽²⁵⁾ fitted the Bunsen coefficient data of Carpenter⁽²⁰⁾ and Murray and Riley,⁽²²⁾ for both pure water and seawater, to a three-term series in the temperature of the Valentiner form, with additional terms for the effect of salinity. The Weiss values are often used for oceanographic and other purposes.

During the development of the new apparatus and procedures to be described below, many preliminary measurements were carried out on several gases to test for random and, especially, systematic errors. Although we now know there was a systematic error in those preliminary determinations (see Appendix A), and although they were crude compared to the measurements now possible, analyses of the data from them, and from Murray, Riley, and Wilson,^(26,27) led Benson and Krause⁽²⁸⁾ to propose series of the form

$$\ln k = a_0 + a_1/T + a_2/T^2 + a_3/T^3 + \dots \quad (2)$$

for the variation of k with temperature. Himmelblau⁽²⁹⁾ had considered a function of this form, but discarded it in favor of a general six-term equation of the second degree in $\ln k$ and $1/T$. Benson and Krause found that a simple three-term series in $1/T$ not only fitted the preliminary data better than other expressions, but also led to the recognition of probable relationships between the molecular properties of the pure gases and the thermodynamic properties of their solutions.

Relatively little is known about the isotopic fractionation of gases during solution. It was first observed by Klots and Benson⁽³⁰⁾ in studies of oxygen and nitrogen. For each gas it was found that the heavier molecular species ($^{34}\text{O}_2$ or $^{29}\text{N}_2$) was more soluble than the respective lighter one ($^{32}\text{O}_2$ or $^{28}\text{N}_2$) by approximately 0.8 per mil at 0°C, and the effect decreased to approximately 0.55 per mil at 27°C. Polgar⁽³¹⁾ obtained results for argon that were roughly comparable, and Weiss⁽³²⁾ observed the larger effect (approximately 10 per mil) to be expected for helium. Kroopnick and Craig⁽³³⁾ found an

effect with oxygen dissolved in seawater that was similar to the results of Klots and Benson in pure water. None of these measurements was precise enough to provide quantitative information about the variation of the isotopic fractionation with temperature and salinity. Muccitelli and Wen⁽³⁴⁾ measured the solubility of D_2 in pure water. By combining their results with those of Crozier and Yamamoto⁽³⁵⁾ for H_2 in pure water, they found the fractionation ranged from approximately 86 per mil at 0°C to 65 per mil at 30°C. To carry out these calculations they first fitted each set of data separately to the generalized Valentiner equation [Eq. (1)] to obtain smooth curves.

The work reported here is the first in a series designed to produce very accurate values for the solubility and isotopic fractionation of gases in pure water from 0 to 60°C. These will reveal the dependence of solubility on temperature, yield information for a better understanding of molecular interactions in liquid water, and provide reference values for geochemical work. We have chosen to study oxygen first, to permit comparison of results from the new method with the best previous determinations.

2. EXPERIMENTAL METHODS AND THEORY

2.1. The Henry Coefficient

The essential features of any apparatus for determination of gas solubility are provision for equilibration of the desired gas and liquid, and means for finding the fugacity of the gas in the vapor phase and the mole fraction of the dissolved gas in the liquid phase. We have used several different equilibration arrangements. The best, and the one used for the measurements reported here, is shown in Fig. 1. A brief description of the equilibrator used in the preliminary work⁽²⁸⁾ is given in Appendix A, with a discussion of evidence suggesting that potential problems are associated with methods of equilibration that involve thin films of liquid.

The equilibration system in Fig. 1 consists of four parts, the spherical equilibrator, the centrifugal pump, the vapor-phase sample bulb, and the liquid-phase sample bulb. The vapor-phase sample bulb is attached by means of a 14/35 standard taper joint. Silicone vacuum grease is used to seal both the joint and the 4-mm pressure-type stopcock on the bulb. The other joints utilize standard O-ring compression, with O-rings made of ethylene-propylene rubber. The equilibrator is composed of concentric spheres with inner and outer volumes of 1 and 2 liters, respectively. The reentrant connection to the inside of the inner sphere provides a compact way of including a relatively large volume for the vapor phase, so that dissolution reduces the pressure less, especially with the more soluble gases. For very expensive gases this feature is deleted. The pump employs a Teflon-covered magnetic stirring bar as an

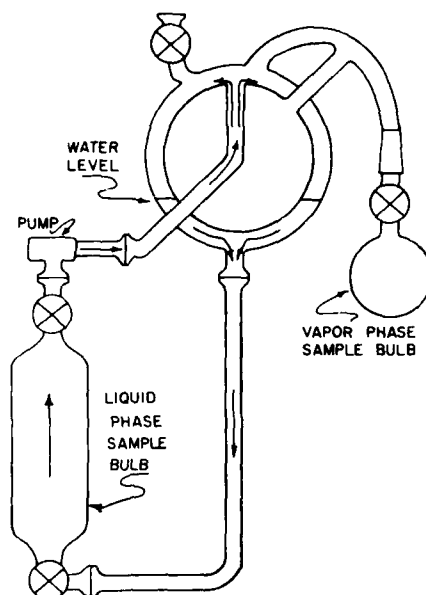


Fig. 1. Glass apparatus for equilibration of gases with liquids, with spherical equilibrator, centrifugal pump, and vapor-phase and liquid-phase sample bulbs. Arrows indicate the direction of liquid flow.

impeller. The stopcocks on the liquid-phase sample bulb are of the Teflon plug type (Ace #8194), but with the Teflon plugs replaced by special ones of either Type 304 stainless steel or glass, with O-ring seals designed to make possible isolation of a very accurately known and reproducible volume in the bulb when the stopcocks are closed. For measurements below room temperature, a small O-ring sealed piston-cylinder is set into the wall of the bulb above the lower stopcock. When released, after volumetric sampling, this permits expansion of the solution to occur when the bulb is removed from the bath. The whole assembly is clamped in a frame of welded stainless steel tubing.

Distilled water from a central stainless steel still is redistilled in a glass system (Corning Model AG-1b). The resulting water has a resistivity greater than $1.5 \text{ M}\Omega\text{-cm}$. Variations in the isotopic constitution of natural waters are too small to have any detectable effect on solubility measurements, even at the level of precision reported here, and no attempt is made to analyze the water isotopically. After the second distillation, the water is degassed in a 2-liter flask to less than 1 ppm of the air that would be dissolved in it at room

temperature, by stirring with a glass-covered magnetic stirring bar and periodically pumping on the flask through a cold trap. Then with the flask of degassed water attached to the filling port of the equilibrator by means of a "Y" coupling, and after the coupling and the equilibrator are carefully evacuated (and the Teflon-covered magnetic stirring bar in the pump degassed), the water is allowed to flow down into the equilibrator and the liquid-phase sample bulb until the pump is covered and the water level is high enough in the equilibrator so that dripping will not occur later during pumping. Research grade gas (the oxygen supplied by Linde was stated to have a total impurity less than 40 ppm) is introduced through a dry ice-acetone cooled trap and the "Y" coupling in such a way as to minimize backstreaming of water vapor toward the tank of gas.

After closing the filling port, the assembly is entirely immersed in a large constant-temperature bath. The speed of the centrifugal pump is adjusted so that water flows up the central tube and smoothly out over the inner sphere without turbulence. After the desired time interval, a known volume of the gas above the solution is isolated in the vapor-phase sample bulb, and a known volume of the solution is closed off in the liquid-phase sample bulb.

While extraction of the gas dissolved in the water sample is being carried out, the undissolved gas sample is dried in dry ice-acetone and liquid-nitrogen cooled traps and Toepler-pumped into a mercury manometric system designed for this work. The system, including the Toepler pump, is in a thermostatic enclosure that permits access to the manometer but maintains temperature uniformity to 0.01°C and constancy to a few millidegrees over several hours. A special meniscus lighting system makes it possible to determine the position and height of the menisci with an accuracy of 0.01 mm using a Beck Model 1000 cathetometer. The volume of the manometer is easily changed to provide the best compromise between volume and pressure for maximum precision. After measurement, a sample of the gas may be transferred to a bulb for analysis with the mass spectrometer.

To remove the dissolved gas, the liquid-phase sample bulb is attached to one arm of a 2-liter extraction flask containing a glass-covered magnetic stirring bar. The other arm is connected to a dry ice-acetone trap, a liquid-nitrogen trap, and a Toepler pump, in succession, with stopcocks between each section. A roughing pump and a diffusion pump, each trapped for oil vapor, and a thermocouple vacuum gauge reading directly to 2×10^{-4} torr are also connected to the manifold. With the whole manifold fully evacuated, the water in the bulb is allowed to flow downward into the extraction flask. A cross-link between the two arms of the flask makes it possible to Toepler-pump the residual gas in the liquid-phase sample bulb through the drying traps into a gas storage bulb. Then "slugs" of gas are taken from the vigor-

ously stirred extraction flask, dried successively in the two traps, and then Toepler-pumped into the storage bulb. After extraction is complete, the gas is transferred to the manometer and the number of moles is measured.

Henry's law for a two-component system composed of a pure gas and water states that at constant temperature the fugacity of the gas in the vapor phase is proportional to the mole fraction of the gas in solution, i.e.,

$$f = k \frac{n_g}{n_w + n_d} \quad (3)$$

where k is the Henry coefficient, and n_d and n_w are the numbers of moles of dissolved gas and water, respectively, in a volume V_s of solution, i.e., the volume of the liquid-phase sample bulb. From the manometric measurements, P_d , V_d , and T_d , on the dissolved gas, we obtain

$$n_d = \frac{P_d V_d}{RT_d Z_d} \quad (4)$$

where Z_d is the compressibility factor for the pure gas at P_d and T_d .

The volume of the solution, V_s , is equal to the volume of the pure water in it plus the partial molal volume of the gas times n_d , i.e.,

$$V_s = \frac{n_w M}{\rho} + \bar{v}_d n_d$$

where M is the molecular weight of water and ρ is its density at the equilibrium temperature T . With algebraic rearrangement,

$$\frac{n_d}{n_w + n_d} = \frac{M}{\rho V_s} \frac{P_d V_d}{RT_d Z_d} \quad (5)$$

where

$$V_s = V_s [1 - (\bar{v}_d - M/\rho)(n_d/V_s)] \quad (6)$$

Determination of the fugacity is slightly more involved. For the moment we shall assume that the Lewis and Randall rule may be applied, i.e.,

$$f = \frac{n_u}{n_t} f^* \quad (7)$$

where n_u is the number of moles of undissolved gas in the volume V_b of the vapor-phase sample bulb, and n_t is the total number of moles of gas and water vapor in that volume. The quantity f^* is the fugacity that the pure gas would have at the equilibrium temperature if its pressure were the same as the total pressure P_t of the gas and water vapor. Therefore,

$$f^* = P_t \exp \left[- \int_0^{P_t} \frac{1 - Z}{P} dP \right] = P_t \exp[-\theta P_t]$$

because for low pressures $Z \approx 1 - \theta P$, where θ is determined by the second virial coefficient of the pure gas. If the exponential is expanded as a power series with higher-order terms neglected, we have

$$f^* = P_t(1 - \theta P_t) = P_t Z^* \quad (8)$$

where Z^* would be the compressibility factor for the pure gas at the equilibrium temperature and the total pressure P_t . If Z_t is the compressibility factor for the vapor phase,

$$P_t = \frac{n_t R T Z_t}{V_b} \quad (9)$$

Furthermore, from the manometric measurements on the undissolved gas,

$$n_u R = \frac{P_u V_u}{T_u Z_u}$$

Substituting this and Eqs. (8) and (9) into Eq. (7) yields

$$f = \frac{P_u V_u}{T_u Z_u} \frac{T}{V_b} Z_t Z^* \quad (10)$$

We may write

$$Z_t Z^* = (1 - \theta_t P_t)(1 - \theta P_t)$$

where θ_t is determined by the second virial coefficient of the gas-water vapor mixture. If the term $\theta_t \theta P_t^2$ is neglected, and we define $\theta' \equiv \theta_t + \theta$, we have

$$Z_t Z^* = 1 - \theta' P_t \quad (11)$$

and

$$f = \frac{P_u V_u}{T_u Z_u} \frac{T}{V_b} (1 - \theta' P_t) \quad (12)$$

Substituting Eqs. (5) and (12) into Eq. (3) yields

$$k = \left[\frac{R}{M} \frac{n_u R}{n_d R} \frac{V'_s}{V_b} \rho T \right] (1 - \theta' P_t) \quad (13a)$$

or

$$k = \left[\frac{R}{M} \frac{P_u V_u}{P_d V_d} \frac{T_d Z_d}{T_u Z_u} \frac{V'_s}{V_b} \rho T \right] (1 - \theta' P_t) \quad (13b)$$

If the molecules in the vapor phase did not interact with each other, i.e., if the vapor phase behaved like an ideal gas, then $Z_t = Z^* = 1$ and $\theta_t = \theta' = 0$, and the measured quantity in brackets in Eqs. (13a) and (13b) would be a constant equal to the Henry coefficient. With molecular attraction occurring in the vapor phase, however, one would expect the ratio $n_u R / n_d R$ to be larger

than for the ideal-gas situation and, correspondingly, the factor $(1 - \theta'P_t)$ would be less than unity. Nevertheless, if accurate values were known for both θ and θ_t , Eq. (13) could be used to calculate k from the measured quantities including P_t .

For the work reported here, a more direct empirical approach has proved to be more fruitful. Suppose Eq. (13a) is rewritten as

$$\left[\frac{R}{M} \frac{n_u R}{n_d R} \frac{V'_s}{V_b} \rho T \right] = k(1 + \theta'P_t) \quad (14)$$

where, again, the fact that $\theta'P_t \ll 1$ has been used. Equation (14) predicts that at a fixed temperature the quantity in brackets should be a linear function of P_t , with k the intercept when P_t is extrapolated to zero. By making such a plot versus pressure at several temperatures, the variation of θ' with temperature may be found empirically. Then one set of measured quantities, including P_t , permits calculation of k .

It is interesting to note that Eq. (14) can be obtained without invoking the Lewis and Randall rule [Eq. (7)] and without carrying the real-gas corrections throughout the analysis, except in the manometry. Suppose it is first assumed that the vapor behaves like an ideal gas. This leads to an equation of the same form as Eq. (14), but without the factor $(1 + \theta'P_t)$. Then recognizing that the real-gas behavior of the vapor phase makes the quantity in brackets depend slightly upon P_t , that quantity can be expanded as a Taylor series in P_t . Equation (14) is the result if terms in higher powers of P_t are negligible.

This method for solubility determinations has many good features. In the first place, it yields fully corrected values for k at essentially infinite dilution, the ideal condition for the validity of Henry's law. The method is straightforward and involves measurements that can be made with both very high precision and accuracy. Negligible error is introduced into k if the approximate expression

$$P_t = \frac{n_u RT Z_e}{V_b} + P_{wv} \quad (15)$$

is used for P_t in the small correction term. The quantity P_{wv} is the saturated vapor pressure of water at the temperature of equilibrium, and Z_e is the compressibility factor for the pure gas at its equilibrium partial pressure. Equation (15) assumes that the gas and water molecules do not interact in the vapor phase. No other corrections for water vapor are required, because all manometric measurements are made on dry gases.

It is not necessary to have accurate values for the partial molal volume of gases with low solubilities because the difference between V'_s and V_s is very small. With oxygen, for example, the largest difference is approximately

30 ppm (at 0°C and 1 atm). In fact, with the empirical approach discussed in relation to Eq. (14), negligible error is introduced by substituting V_s for V'_s . This may be seen from Eq. (6): $V'_s = V_s[1 - (\bar{r}_d - M/\rho)(n_d/V_s)]$ is approximately equal to $V_s[1 - (\bar{r}_d - M/\rho)\beta(P_t - P_{wv})]$, where β is the Bunsen coefficient and $\beta(\bar{r}_d - M/\rho) \equiv \gamma$ is a constant at a given temperature. After substitution for V'_s in Eq. (14) and rearrangement, one obtains

$$\left[\frac{R}{M} \frac{n_u R}{n_d R} \frac{V_s}{V_b} \rho T \right] = k[(1 - \gamma P_{wv}) + (\gamma + \theta')P_t] \quad (16)$$

Therefore, when the quantity in brackets on the left is plotted versus P_t , part of the V'_s correction is subsumed in the empirical determination of the factor multiplying P_t . Assuming that γP_{wv} is negligible compared to unity (for oxygen from 0 to 60°C, the largest error introduced is only 3 ppm, but even for a more soluble gas like xenon the error would be less than 50 ppm), Eq. (16) becomes

$$k' \equiv \left[\frac{R}{M} \frac{n_u R}{n_d R} \frac{V_s}{V_b} \rho T \right] = k(1 + \lambda P_t) \quad (17)$$

where $\lambda \equiv \gamma + \theta'$.

The design of the experiment minimizes the significance of almost all systematic analytical errors. In Eq. (13b) note that the eight manometric factors occur in ratio pairs. Consequently, if the volume of the vapor-phase sample bulb is chosen so that n_u is approximately equal to n_d , the two sets of manometric measurements are carried out under similar conditions, and systematic errors in the numerator and denominator tend to cancel. The acceleration due to gravity, which is implicit in the pressures, need not be known. The volumes V_s and V_b of the bulbs are determined as a function of temperature by mercury weighing. For the density of mercury we use the values given by Bigg,⁽³⁶⁾ but again, as in the pressure measurements, any possible systematic error would cancel. Even the effect of small amounts of gas impurities tends to cancel if the solubilities of the impurities are not too different from that of the gas being studied.

In Eq. (17) the uncertainty in the gas constant R is approximately 30 ppm (Sengers *et al.*⁽³⁷⁾), and the errors in M and ρ are less than 5 ppm. The equilibrium temperature is measured with a quartz crystal thermometer (Hewlett-Packard Model 2801A).⁽³⁸⁾ We⁽³⁹⁾ have found that with appropriate calibration, it will measure temperature relative to IPTS-68 with an absolute accuracy of probably 0.003 K and no worse than 0.005°K (approximately 15 ppm). In both the large constant-temperature baths designed for this work, control varies from ± 0.001 K at lower temperatures to ± 0.003 K (10 ppm) at 60°C. The crystal thermometer probe is located near the equilibrator in

the bath, and tests show the maximum difference in temperature between the bath and the solution in the equilibrator is no greater than 0.002 K (7 ppm). For oxygen between 0 and 60 °C, an error of no more than 80 ppm is introduced by assuming there is no difference between IPTS-68 and the thermodynamic temperature scale.

The liquid-phase bulbs have volumes of 800 to 900 cm³ with an uncertainty less than 10 ppm. As discussed above, the smaller vapor-phase bulbs are chosen in size according to both the gas and the temperature to make n_u approximately equal to n_d . For oxygen the maximum error in V_u varies from 20 ppm at 0 °C to 40 ppm at 60 °C. The precision of the manometric determinations of $n_u R$ and $n_d R$ depends upon the amount of gas and therefore, for approximately fixed V_u , upon both the gas and the temperature. Each gas sample is measured twice, with the gas expanded and recompressed between analyses to make them independent. Twice the standard deviation of the percentage difference of the two measurements from each other for a number of samples provides a useful indication of the manometric precision. For oxygen it ranges from 40 ppm (0 °C) to 80 ppm (60 °C).

From these estimates we might expect measurements of T , V_u , V_b , $n_u R$, and $n_d R$ to lead to a total random analytical error in k of roughly 0.01‰ at low temperatures and 0.02‰ at 60 °C. The total systematic analytical error from R , M , ρ , and T , assuming the worst-case situation, should be less than 0.012‰.

The extraction and gas processing procedures have been tested exhaustively. For example, although the partial pressures in the drying manifolds do not exceed the saturated vapor pressure of most gases at the temperature of liquid nitrogen, tests are carried out with each gas to show that it is not condensed in the trap. No gas is mechanically captured in the dry ice trap by freezing water vapor. We have found that drying successive slugs of gas, which transfers relatively little water to the trap, is preferable to pumping straight through and thereby transferring large quantities of water. In another test, measured quantities of gas in a manometer bulb are transferred to the input of the extraction vessel, where the liquid-phase sample bulb normally is attached. With gas-free water in the extraction vessel, the gas is let into the vessel and, after stirring, the gas is extracted in the normal manner. When it is measured, it agrees with the initial amount. In a different test for possible losses of gas in the processing, a measured quantity of gas in the manometer is pumped with an extraction manifold Toepler pump into its storage bulb. When the gas is pumped back into the manometer with the Toepler pump in the manometric system and remeasured, no significant change in the number of moles is detectable after one such cycle, even if the gas is left in the storage bulb overnight. Repeated cycling of this kind does show that for oxygen an average loss of approximately 30 ppm per cycle occurs, but even if this were

detectable in the manometer, the errors in the dissolved and undissolved gas sample determinations would at least partly cancel as discussed earlier.

In summary, with good, clean, high-vacuum technique, including simple standard vacuum tests before and after processing a gas sample, the whole operation of extracting, handling, and measuring the gas is straightforward, reliable, and quantitative.

The equilibrator has been tested thoroughly in a variety of ways. For the large volume of liquid involved (approximately 1.5 liters), the rate of equilibration is relatively rapid. Although the design of the filling arrangement does not permit accurate short-term kinetic studies, equilibrations over longer periods of time suggest that at 5°C and the normal pumping speed of 800 $\text{cm}^3 \text{min}^{-1}$, the half-time for equilibration is 4 or 5 min. This corresponds to approximately 2 to 2.5 cycles of the liquid through the system. Equilibration periods of from 4 to 116 h yield identical results within analytical error, indicating both achievement of equilibrium and absence of vacuum problems. Mass spectrometric tests show no growth of impurities in the gas during either equilibration or later storage in glass sample tubes before the isotopic analyses. (It should be noted, however, that silicone vacuum grease is imperative when storing oxygen for even a short time interval. Other greases are oxidized, with accompanying fractionation of the oxygen isotopes.) Equilibration is slower at high temperatures because the fourfold decrease of the viscosity reduces both the pumping action of the pump and mixing within the liquid-phase sample bulb. An overnight equilibration period of 20 h has been found to be convenient for all but the highest temperatures, where 44 h is used.

Although varying the pumping speed over the range 500 to 900 $\text{cm}^3 \text{min}^{-1}$ does affect the rate of equilibration, it does not change the results for k . The pumping speed is chosen primarily to produce very stable, non-turbulent flow. In normal operation it is so smooth that it is difficult to observe the flow of water over the inner sphere. Approach to equilibrium from the supersaturated state (achieved by first equilibrating at a lower temperature) leads to values for k that are identical with those from the undersaturated state. Several equilibrator units have been used, including ones without the expansion cylinder and one using greased stopcocks on the liquid-phase sample bulb. Although all give the same results within analytical error, the greased unit is not used because the grease makes it difficult to keep the system clean.

All tests have shown the equilibrator to be extremely reliable. The design eliminates the thin-film problems discussed in Appendix A, and yields values of k for the bulk liquid. We believe that there are no systematic errors associated with it and that the accuracy of the results is determined by the precision of the analytical measurements.

2.2. Isotopic Fractionation

The equilibrium isotopic fractionation factor α for the solution of $^{34}\text{O}_2$ and $^{32}\text{O}_2$ is defined as the abundance ratio of the two molecules in the dissolved gas to the corresponding ratio in the gas above the solution. In the notation employed above,

$$\alpha \equiv \frac{{}^{34}n_d/{}^{32}n_d}{{}^{34}n_u/{}^{32}n_u} \equiv \frac{r_d}{r_u} \quad (18)$$

With algebraic rearrangement and the use of Eq. (17), this becomes

$$\alpha = \frac{{}^{32}k}{{}^{34}k} \quad (19)$$

[Negligible error is introduced by assuming that the factor $(1 + \lambda P_i)$ is the same for the two molecular species.] Consequently, measurement of the isotopic fractionation factor yields the ratio of the Henry coefficients for the two gases.

Mass spectrometric techniques make it possible to determine α with very high accuracy. Ion beams produced from the two isotopic molecules are simultaneously collected in separate Faraday cups, and a quantity P , proportional to their ratio, is measured with a voltage divider in a null arrangement. Then by feeding the undissolved and dissolved gases alternately into the mass spectrometer ion source, a direct determination of the difference $\Delta P = P_d - P_u$ is made. From

$$\delta \equiv \alpha - 1 = \frac{r_d - r_u}{r_u} = \frac{\Delta P}{P_u} \quad (20)$$

δ and α can be calculated. Systematic effects like ion-source discrimination tend to cancel, and with appropriate techniques the precision and accuracy usually are limited by noise. For the work reported here, the values of δ lie within the range 0.5 to 0.9 per mil and, from repeated mass spectrometric measurements on the same pair of gas samples and on gases from separate equilibrations at essentially the same temperature, the precision is better than 0.02 per mil. This means that the ratio $\alpha = {}^{32}k/{}^{34}k$ can be measured with an error less than 20 ppm, and the uncertainty in the values for ${}^{34}k$ is determined by the accuracy of ${}^{32}k$ rather than by the mass spectrometry.

For the isotopic measurements we used a modified version of the single-focusing, 60° magnetic sector mass spectrometer described by Nier.⁽⁴⁰⁾ It is equipped with a dual system⁽⁴¹⁾ for rapid interchange of samples into the ion source, and the mass spectrometer tube is designed to permit null measurements for pairs of ions with mass ratios up to 3/2 by insertion of the appropriate dual collection system. To measure small isotopic effects of the kind

reported here, it is important that the mass spectrometric analyses be made twice, one immediately after the other, with the gas samples exchanged between the two sample systems between analyses. This compensates for possible differences in the fractionation caused by the capillary leaks, and for the minute differences in the background contaminations from the sample systems. Although the latter effect normally is small, we have found that, even with a very "clean" spectrometer, it usually is the more significant source of potential error. The average correction in the oxygen measurements to be reported here was only 0.007 per mil, but in isotopic analyses of some other gases, corrections up to 0.05 per mil have been required.

3. RESULTS AND DISCUSSION

3.1. Data

According to Eq. (17), at fixed temperature, k' should be a linear function of P_t with intercept k and slope $k\lambda$. We have made sets of measurements of k' vs. P_t for oxygen at each of four temperatures, 0, 15, 35, and 55°C. Two of these are illustrated in Fig. 2, where it is evident that within experimental error the relationships are linear over the indicated pressure ranges. Although the value of λ at each temperature can be calculated directly from the ratio of the slope of the line to its intercept, it is useful to replot the data as k'/k vs. P_t because the slopes of the resulting lines are the values of the corresponding

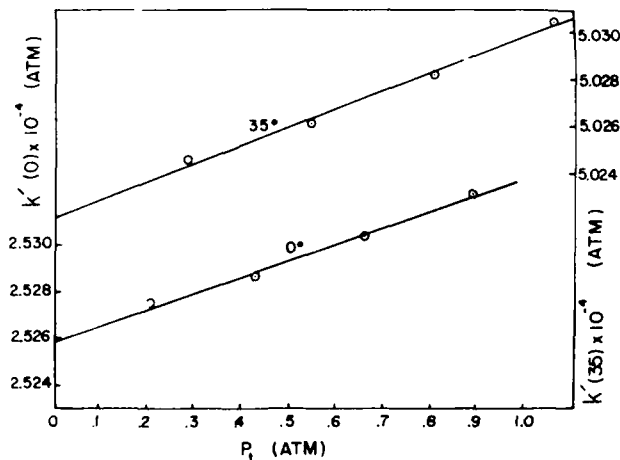


Fig. 2. Graphs of k' vs. P_t at 0 and 35°C.

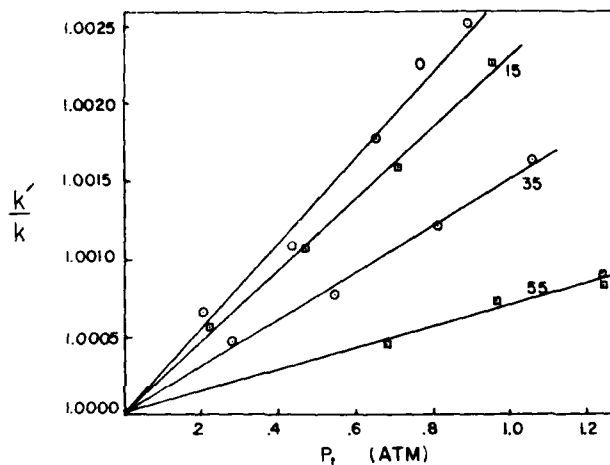


Fig. 3. Graphs of k'/k vs. P_t at 0, 15, 35, and 55°C.

λ 's. This is shown in Fig. 3, where it is clear that λ decreases as the temperature increases. Furthermore, a graph of λ vs. t is linear according to

$$\lambda = 0.002805 - 0.0000375t \quad (21)$$

where t is in degrees Celsius. The reason for this empirical result is not obvious. Recall that if one uses the Lewis and Randall rule, $\lambda \equiv \gamma + \theta_t + \theta$. Furthermore, γ is small. Therefore, because values for θ calculated from the second virial coefficient for oxygen between 0 and 60°C, given by Sengers *et al.*,⁽³⁷⁾ fit approximately the function

$$\theta = 0.000975 - 1.426 \times 10^{-5}t + 6.436 \times 10^{-8}t^2 \quad (22)$$

it is surprising that λ should be linear in t . With λ known as a function of t , Eq. (17) can be used to find k at any temperature from a single set of measurements at any total pressure. Experimental results for k and δ from 0 to 60°C are given in Table I. As noted earlier, we believe these values for k range in accuracy from approximately 0.01% at 0°C to 0.02% at 60°C, and the values for δ are probably good to better than 0.02 per mil.

3.2. The Variation of the Henry Coefficient with Temperature

It is interesting to examine empirically how various functions fit the accurate data presented here. The results for several types of series are shown in Table II. The data have been fitted to each of the series by straightforward

Table I. Experimental Values

t (°C)	k' (atm $\times 10^{-4}$)	P_t (atm)	k (atm $\times 10^{-4}$)	σ_k , deviation of k from fit	$\delta_{34/32}$ $\times 10^3$	Deviation of δ from fit $\times 10^3$
0.046	2.53491	0.8060	2.52918	-0.016	0.820	-0.012
0.052	2.53525	0.8067	2.52951	-0.020	0.838	0.006
1.001	2.60302	0.8014	2.59725	-0.006	0.810	-0.017
1.002	2.60385	0.8060	2.59804	0.022	0.826	-0.001
1.998	2.67478	0.8117	2.66885	0.008	0.816	-0.005
2.000	2.67463	0.8111	2.66870	-0.003	0.809	-0.012
3.003	2.74687	0.8139	2.74085	-0.002	0.820	0.004
4.003	2.81967	0.8243	2.81350	0.011	0.859	0.048
4.997	2.89190	0.8178	2.88571	0.012	0.787	-0.018
6.006	2.96540	0.8307	2.95904	0.003	0.821	0.021
7.000	3.03867	0.8323	3.03224	0.018	0.795	0.000
8.000	3.11181	0.8365	3.10529	0.006	0.781	-0.009
10.001	3.25864	0.8446	3.25195	-0.015	0.812	0.032
12.000	3.40698	0.8501	3.40016	0.005	0.749	-0.020
13.999	3.55470	0.8618	3.54772	0.004		
15.002	3.62863	0.8744	3.62152	0.000	0.747	-0.007

16.003	3.70206	0.8687	3.69497	-0.007	0.774	0.025
20.003	3.99447	0.8871	3.98719	-0.014	0.744	0.015
21.998	4.13953	0.8863	4.13213	0.004	0.688	-0.032
24.001	4.28145	0.9135	4.27400	-0.030	0.738	0.028
24.002	4.28125	0.9118	4.27381	-0.036	0.718	0.008
26.999	4.49322	0.9254	4.48577	-0.012	0.668	-0.027
30.001	4.70243	0.9459	4.69496	0.047	0.682	0.001
30.004	4.70097	0.9361	4.69358	0.014	0.674	-0.007
33.003	4.90119	0.9538	4.89287	-0.012	0.655	-0.012
36.003	5.09545	0.9775	5.08821	0.011	0.636	-0.017
38.998	5.28129	0.9928	5.27426	-0.004	0.633	-0.007
42.000	5.46237	1.0170	5.45555	0.027	0.631	0.005
44.998	5.63289	1.0466	5.62631	0.018	0.625	0.012
47.996	5.79427	1.0720	5.78804	0.001	0.602	0.002
48.000	5.79333	1.0681	5.78712	-0.018	0.606	0.006
50.999	5.94724	1.0925	5.94146	-0.009	0.591	0.004
53.991	6.09083	1.1284	6.08549	-0.014	0.561	-0.013
57.000	6.22628	1.1617	6.22147	-0.010	—	—
57.001	6.22789	1.1573	6.22310	0.015	0.568	0.007
59.993	6.35334	1.1959	6.34915	0.024	0.553	0.004
59.998	6.35056	1.1831	6.34642	-0.023	0.545	-0.004

Table II. Percent Standard Deviations of k when the Experimental Values for $\ln k$ and T Are Fitted to Series of Various Forms and Numbers of Terms

Form	Number of terms			
	3	4	5	6
$\sum 1/T$	0.0176	0.0178	0.0178	0.0164
$\sum 1/\ln T$	0.1338	0.0181	0.0178	0.0163
Valentiner ^a	0.1358	0.0193	0.0181	0.0164
$\sum \ln T$	0.2167	0.0197	0.0180	0.0163
$\sum T$	0.4887	0.0421	0.0191	0.0164

^a The Valentiner series is Eq. (1).

matrix-inversion techniques⁽⁴²⁾ on a time-sharing terminal of a CDC Cyber 74 computer. In each case we have used from three to six terms in the expansion, and then examined the resulting standard deviations. It is evident that the power series in $1/T$ provides by far the best fit. In fact, the three-term expansion in $1/T$ fully fits the data, i.e., additional terms provide no improvement and the precision of fit is comparable to the precision of the measurements. For all the other types of series at least four terms are required, and further improvements are achieved by adding a fifth term. In a related test the data have been fitted to three-term power series in $1/T^x$, i.e.,

$$\ln k = a_0 + a_1/T^x + a_2/(T^x)^2 \quad (23)$$

Figure 4 shows the variation of the percentage standard deviation of the data from each series as a function of the parameter x . The minimum deviation occurs with x very nearly equal to unity ($x_{\min} = 0.99$)!

The Valentiner series, Eq. (1), is an integrated van't Hoff equation that in one form or another has been employed for many years to express the temperature dependence of equilibrium constants. In 1966, Clarke and Glew⁽²³⁾ presented a generalized treatment of the integration with an excellent discussion of the evaluation of the errors in the standard thermodynamic-function changes when Eq. (1) is used to fit experimentally determined equilibrium constants. In their formalism, Eq. (1) follows from an expansion of the standard enthalpy change ΔH° in a Taylor series in T about a reference temperature θ . As such it is undeniably an appropriate expression for fitting experimental data. More is claimed for this expression, however. Clarke and Glew state that "only those equations equivalent to [Eq. (1)] furnish the unique, best unbiased estimates of the standard thermodynamic-function changes for reactions." This is too sweeping. Thermodynamic arguments alone cannot lead one to predict the otherwise unknown temperature

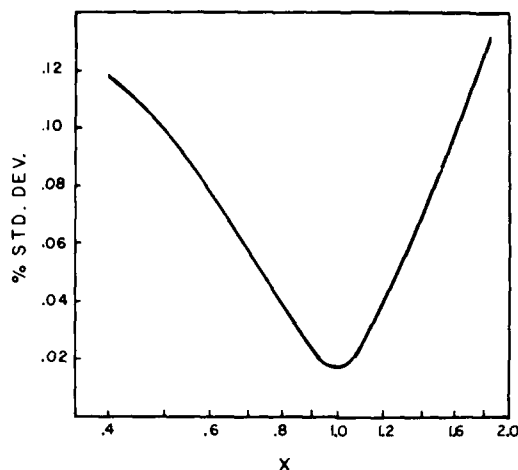


Fig. 4. Variation of the percentage standard deviation of the data from the equation $\ln k = a_0 + a_1/T^x + a_2/(T^x)^2$ as a function of the parameter x . Minimum deviation occurs at $x = 0.99$.

dependence of equilibrium constants. The danger in prescribing one functional form is that it may discourage the use of other, simpler, and *equally valid* forms which may give more insight into the underlying phenomena.

In Appendix B we show that Eq. (2), the power series in $1/T$, may be derived in a manner that is *identical* to that given by Clarke and Glew for Eq. (1), except that a different measure of temperature, $1/T$, is used in place of T . (One could argue that $1/T$ is fundamentally just as good a measure of temperature as T , or even better because it occurs more naturally in statistical mechanics.) Expansion of ΔH° in a Taylor series in $1/T$ about the reciprocal reference temperature $1/\theta$, use of the thermodynamic relationships, and algebraic manipulation lead directly to Eq. (2). The coefficients in this series are as simply related to the standard thermodynamic difference functions as are the coefficients in Eq. (1), and the method for determining the functions and their standard errors is completely analogous. Thus, the type of argument that leads to Eq. (1) does not produce it uniquely. Equation (2) and other similarly consistent possibilities are on equal thermodynamic footing with Eq. (1).

On the basis of thermodynamic consistency, ability to fit accurate data, and simplicity, Eq. (2), the power series in $1/T$, is clearly the best family of functions proposed to date for representing the variation of k with T . Over the range of temperature studied here, its three-term member,

$$\ln k = a_0 + a_1/T + a_2/T^2 \quad (24)$$

is sufficient to fit the solubility data that presently are available. Values for the three coefficients for oxygen are given in Table VI. It remains to be seen whether there is a fundamental significance to Eq. (24). The idea seems to be supported by the relationships between the molecular properties of the noble gases and the parameters of their solutions, which emerged from the analysis of the preliminary data.⁽²⁸⁾ Below, we shall see that the present results for oxygen are in accord with that analysis.

Although the solubility measurements reported here apparently are the most accurate determinations ever made of the equilibrium constant for any reaction over a wide range of temperature, their excellent fit to Eq. (2) does not necessarily imply that the equation should be applicable to other kinds of reactions where the interaction mechanisms are different. We have explored the literature for the best data on equilibrium constants for other types of systems such as weak acids and bases in water. Most of the data are either too imprecise or too limited in temperature range to distinguish between the ability of Eqs. (1) and (2) to fit them. For the few relatively accurate results available, viz. the work of Feates and Ives⁽⁴³⁾ and Ives and Marsden⁽⁴⁴⁾ on weak acids, Eq. (2) gives the better fit, and again only the three-term equation (24) is required, while use of Eq. (1) requires four terms. These results suggest that Eq. (24) [or, more generally, Eq. (2)] may have broader applications than for gas solubilities, but precise data for a number of other systems are needed to test this possibility.

3.3. Comparison with Previous Measurements

The fifth column of Table I gives the percentage deviations of the new data for the Henry coefficient of oxygen from their fit to Eq. (24), the three-term power series in $1/T$. These are illustrated graphically in Fig. 5, where the new data are represented by the solid circles distributed along the reference line. For comparison with probably the best previous determinations, we have recalculated the experimental values of Montgomery, Thom, and Cockburn,⁽¹⁷⁾ Murray and Riley,⁽²²⁾ Klots and Benson,⁽¹⁶⁾ and Carpenter⁽²⁰⁾ to give values for k with appropriate corrections to make them correspond as nearly as possible to our values. The results are included in Fig. 5. The very high precision of the new results is evident, but another observation is equally significant. Visual inspection indicates that the five sets of results are in excellent agreement, with the four older sets of data points scattered more or less equally on either side of the smoothed curve for the new data. Table III illustrates this in another way. The rms percentage deviation for the new data is more than an order of magnitude smaller than that for any of the other four sets of data. The percentage deviations of the Klots and Benson set, the Carpenter set, and the Montgomery *et al.* set average almost to zero, indi-

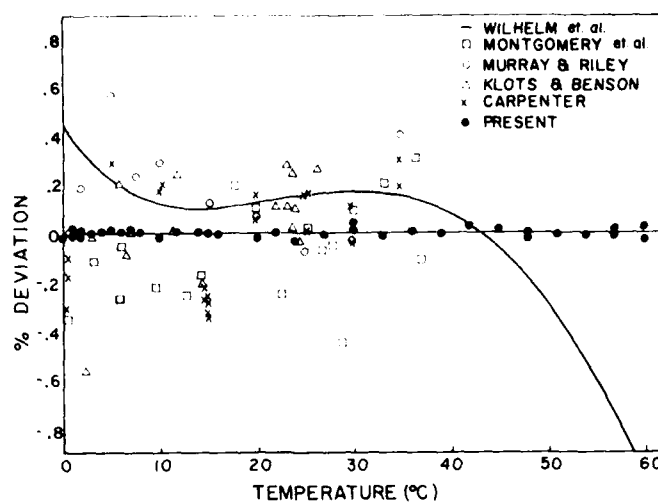


Fig. 5. Variation with temperature of the percentage deviation of the new measurements for k , and of the best previous data for oxygen, from the equation $\ln k = 3.71814 + 5595.17/T - 1049668/T^2$. The smooth curve of Wilhelm *et al.* (ref. 3) is also shown.

cating each is equally scattered about the new fit, while the values of k from Murray and Riley average 0.18% higher.

This agreement is very important, because it suggests that the results are probably free from systematic errors well within the random errors in the older data. On the basis of our own tests, as discussed in Section 2.1, we believe the accuracy of the new technique is determined by the random errors, i.e., approximately 0.01 to 0.02%, but the agreement with the best

Table III. Comparison of the Deviations of Data from Various Sources with the Present Results

Source	$\frac{\sum \sigma_{\%} \text{ deviation}}{n}$	$\left[\frac{\sum (\sigma_{\%} \text{ deviation})^2}{n} \right]^{1/2}$
Murray and Riley ^a	+0.180	0.264
Klots and Benson ^b	+0.042	0.212
Carpenter ^c	-0.024	0.220
Montgomery, Thom, and Cockburn ^d	-0.079	0.215
Present	0	0.017

^a See ref. 22.

^b See ref. 16.

^c See ref. 20.

^d See ref. 17.

previous solubility measurements on any gas adds confidence to that judgment. This independent confirmation of the method is significant also for results we shall report later on other gases, because for them the previous data are of lower quality than for oxygen and no significant comparison with the new results will be possible.

The curve obtained by Wilhelm, Battino, and Wilcock⁽³⁾ by fitting selected data to a four-term series of the Valentiner type, Eq. (1), is included in Fig. 5. The comparison is not significant with respect to the merits of Eq. (1) relative to Eq. (2) because other less accurate data⁽¹¹⁾ were used by Wilhelm *et al.* for the high-temperature region, but it is clear that above 40°C their smoothed values become quite incorrect.

3.4. Thermodynamic Properties of the Solution

For systems of this kind, the standard state of the gas in the vapor phase at any temperature is usually defined to be that in which the gas has a fugacity of 1 atm, while the standard state for the dissolved gas at any temperature is the hypothetical state found by extrapolating the line representing Henry's law on an f vs. x graph to unit mole fraction for the dissolved gas. With these choices, and Eq. (24), the changes in the partial molal thermodynamic functions are

$$\Delta\bar{G}^\circ = R[a_0T + a_1 + a_2/T] \quad (25)$$

$$\Delta\bar{H}^\circ = R[a_1 + 2a_2/T] \quad (26)$$

$$\Delta\bar{S}^\circ = R[-a_0 + a_2/T^2] \quad (27)$$

and

$$\Delta\bar{C}_p^\circ = -2Ra_2/T^2 \quad (28)$$

[Note that these differ in sign from those given earlier⁽²⁸⁾ because $\ln k$, rather than $\ln(1/k)$, has been used in Eq. (24).] Values for $\Delta\bar{G}^\circ$, $\Delta\bar{H}^\circ$, $\Delta\bar{S}^\circ$, and $\Delta\bar{C}_p^\circ$ are given at four temperatures in Table IV, with numbers calculated by Wilhelm, Battino, and Wilcock⁽³⁾ and the theoretical predictions of Pierotti.⁽⁴⁵⁾ The percentage standard deviation in our values for $\ln k$ (and, therefore, $\Delta\bar{G}^\circ$) is 0.0016%. This leads to a random error in $\Delta\bar{C}_p^\circ$ equal to 0.15%, with a 95% confidence level. As would be expected from Fig. 5, the improvements over the Wilhelm *et al.*⁽³⁾ results are small except for $\Delta\bar{C}_p^\circ$ and at higher temperatures. The Pierotti values are systematically below the experimental ones, with $\Delta\bar{C}_p^\circ$ smaller by approximately 30% at 298°K. Reference to Pierotti's paper also shows that the predicted rate of change of $\Delta\bar{C}_p^\circ$ with temperature is only 1/3 the experimental value. It should be noted,

Table IV. Comparison of Values for $\Delta\bar{G}^\circ$, $\Delta\bar{H}^\circ$, $\Delta\bar{S}^\circ$, and $\Delta\bar{C}_p^\circ$ with Literature Values^c

Source	$\Delta\bar{G}^\circ$ (cal-mole ⁻¹)	$\Delta\bar{H}^\circ$ (cal-mole ⁻¹)	$\Delta\bar{S}^\circ$ (cal-°K ⁻¹ mole ⁻¹)	$\Delta\bar{C}_p^\circ$ (cal-°K ⁻¹ ·mole ⁻¹)
283.15°K				
Present	5846.0	-3613	-33.41	52.03
Wilhelm <i>et al.</i> ^a	5847	-3594	-33.34	47.19
298.15°K				
Present	6327.4	-2872	-30.85	46.93
Wilhelm <i>et al.</i> ^a	6328	-2882	-30.89	47.75
Pierotti, theoretical ^b	6270	-2423	-28.5	32.2
313.15°K				
Present	6773.3	-2201	-28.66	42.54
Wilhelm <i>et al.</i> ^a	6774	-2162	-28.53	48.31
328.15°K				
Present	7188.7	-1592	-26.76	38.74
Wilhelm <i>et al.</i> ^a	7184	-1433	-26.26	48.88

^a See ref. 3.^b See ref. 45.^c $R = 1.98717$ cal-°K⁻¹·mole⁻¹.

especially, that Eq. (28) states that $\Delta\bar{C}_p^\circ$ varies inversely with the square of the absolute temperature.

3.5. Solution Parameters and Molecular Properties of the Gases

From analyses of preliminary experimental data for seven gases, Benson and Krause⁽²⁸⁾ found that when the variation of k with T was expressed by Eq. (24), relationships emerged among the solution parameters and the thermodynamic and molecular properties of the gases. This became particularly apparent when Eq. (24) was rewritten in the form

$$\ln k = A_3 \left(\frac{T_1}{T} - 1 \right) + A_2 \left(\frac{T_1}{T} - 1 \right)^2 \quad (24a)$$

and the data were smoothed by requiring that the constant A_2 be the same for all the gases. (Some other parameters are defined in terms of a_0 , a_1 , and a_2 in Table V.) Benson and Krause found that "although the A_2 smoothing slightly increases some values and decreases others, for all parameters the patterns of the numbers are skewed very little in any systematic way." Furthermore, each of the parameters, a_0 , a_1 , a_2 , T_1 , A_3 , and others, became an essentially linear function of $(\epsilon/k_B)^{1/2}$, the square root of the force constant

Table V. Definitions of Some Parameters

$T_1 = -2a_2/[a_1 + (a_1^2 - 4a_0a_2)^{1/2}]$	$A_0 = a_0$
$A_3 = -(a_1^2 - 4a_0a_2)^{1/2}/T_1$	$A_1 = a_1/T_1$
$M = [-a_1^2 + 4a_0a_2]/4a_2$	$A_2 = a_2/T_1^2$
$T_M = -2a_2/a_1$	$A_0 + A_1 + A_2 = 0$

^a T_1 is the absolute temperature at which the Henry coefficient k hypothetically would be unity, if the systems hypothetically had the same properties outside the experimental temperature range.

^b $M = \ln k_{\max}$.

^c T_M is the temperature for maximum k .

of the gas. They concluded, "The implication is strong that with more accurate measurements A_2 and $(\Delta \bar{C}_p)_1$ would be found to be the same for all the gases."

A partial test of this suggestion is possible from a comparison of the values for the parameters obtained here with the corresponding values predicted from the preliminary data smoothed on the assumption that A_2 should be common to all the gases. These are shown in Table VI, together with the preliminary "raw" values. The improvement achieved by the A_2 smoothing process is striking, and it lends support to the idea that Eq. (24a) is a universal solubility equation in the sense that A_2 is common to all the gases with only T_1 and A_3 being characteristic of the specific gas.

Table VI. Comparison of the Values for Various Parameters with the Smoothed and Raw Values Obtained in the Preliminary Work (Reference 28)

Source	$a_0 = A_0$	a_1 ($^{\circ}\text{K} \times 10^{-3}$)	$-a_2$ ($^{\circ}\text{K}^2 \times 10^{-5}$)	T_1 ($^{\circ}\text{K}$)
Present	3.71814 ^a	5.59617 ^a	10.49668 ^a	168.667 ^a
Preliminary, smoothed	3.7671	5.5869	10.5075	168.85
Preliminary, raw	4.0605	5.4167	10.261	168.22

Source	A_1	$-A_2$	$-A_3$	M	T_M ($^{\circ}\text{K}$)
Present	33.179	36.897	40.615	11.177	375.14
Preliminary, smoothed	33.088	36.855	40.622	11.193	376.15
Preliminary, raw	32.200	36.261	40.321	11.209	378.87

^a The three present primary parameters, a_0 , a_1 , and a_2 , and T_1 individually are not accurate to the number of figures given, but they are coupled by the fitting process and it is useful to carry an extra figure for internal consistency in parameter conversion.

Equation (24a) expresses k in terms of the "scaled temperature" T/T_1 . The equation also may be written as

$$\ln k = A_0 + A_1 \left(\frac{T_1}{T} \right) + A_2 \left(\frac{T_1}{T} \right)^2 \quad (24b)$$

which is similar in form to Eq. (24), but here the third term on the right, and therefore $\Delta \bar{C}_p^\infty = -2RA_2(T_1/T)^2$, would be the same for all gases at the same scaled temperature. (Note that because $T = T_1$ when $k = 1$, $A_0 + A_1 + A_2 = 0$, and Eq. (24b) involves only three independent constants.)

3.6. Values for k at Temperatures above 60°C

Values for k at high temperatures, well beyond the range of our determinations, are needed for many purposes. Although measurements that have been reported for temperatures above 100°C are much less accurate, we have attempted to relate them to our work. The result is only partly successful, but at least for the present it provides both the best and easiest way to calculate values for k at elevated temperatures.

To test the ability of our data and Eq. (24) to give correct values when extrapolated to higher temperatures, the data for four different temperature ranges, 0–20, 0–30, 0–40, and 0–60°C, have been fitted separately to Eq. (24) and then used to predict k at temperatures above the range of each set of data. The results are shown in the first four rows of Table VII. (The "extrapolated value" at 60°C for the 0–60°C range is underlined to indicate it is *not* extrapolated.) The predicted or extrapolated values from the data for 0–20, 0–30, and 0–40°C agree extremely well with the measured value at 60°C. For example, the 0–30°C results, when extrapolated to twice the temperature range of the data, disagree with the measured value by only 0.06%.

The most extensive measurements of oxygen solubility at high temperatures and pressures have been those carried out at the Battelle Memorial Institute and included in the report by Stephan, Hatfield, Peoples, and Pray.⁽⁴⁶⁾ They defined k as the ratio of the partial pressure of the gas in pounds per square inch absolute to the solubility in milliliters of gas at STP per gram of solution, in the limit as the partial pressure approaches zero. In the fifth row of Table VII we have reexpressed their results in atmospheres, but their experimental method does not permit calculation of a k that would correspond exactly to the Henry coefficient defined in Eq. (3). Despite the lack of equivalence of the two k 's, it is useful to compare the Battelle experimental results with the values obtained by extrapolating the Eq. (24) fit to our complete set of data for 0–60°C. At 100°C the numbers differ by 1.9%, which is within the uncertainty of their experimental numbers. At higher temperatures, however, the difference becomes progressively greater.

Table VII. Comparison of Values for the Henry Coefficient at Temperatures above 60°C

Source of data	Temp. range of data (°C)	60°C (333.15°K)	100°C (373.15°K)	135°C (408.15°K)	163°C (436.15°K)	204°C (477.15°K)	260°C (533.15°K)	288°C (561.15°K)
Present fitted to Eq. (24)	0-20	6.3256	7.081	Extrapolated value for $k \times 10^{-4}$				
Present fitted to Eq. (24)	0-30	6.3515	7.157					
Present fitted to Eq. (24)	0-40	6.3491	7.149					
Present fitted to Eq. (24)	0-60	6.3480	7.145					
Stephan <i>et al.</i> ^a			7.01	Measured $k \times 10^{-4}$				
Present plus Stephan <i>et al.</i>		6.40	7.07	6.23	5.50	3.88	2.29	1.63
				Eq. (2), four-term fit for $k \times 10^{-4}$				
				6.36	5.37	3.85	2.24	1.68

^a See ref. 46.

The significance of these differences is not clear, but it is interesting to note that application of Eq. (2) with four terms to a combination of the data of Stephan *et al.* for 100–288 C with our data for 0–60 C (with equal weighting for all points despite the disparity in precisions) fits all the Stephan *et al.* data with a rms deviation of 2.0%, which is within their experimental error. Refer to the sixth row in Table VII. Between 0 and 60 C the deviations considerably exceed the uncertainties in our measurements, but they are never greater than 0.7%. The fit to the high-temperature data is better than that given by the more complex Himmelblau⁽²⁹⁾ equation, and calculation of k for a given T is much simpler.

Until more accurate data become available for temperatures above 60 C, we recommend on the basis of the results above that values for k be calculated from one of two equations, depending upon the temperature range involved:

(a) For very accurate values in the temperature range 0–100 C:

$$\ln k = 3.71814 + 5596.17/T - 1049668/T^2 \quad (29)$$

$$\text{where } f = kx \quad (3)$$

(b) For values above 100 C:

$$\begin{aligned} \ln k = & -4.1741 + 1.3104 \times 10^4/T - 3.4170 \times 10^6/T^2 \\ & + 2.4749 \times 10^8/T^3 \end{aligned} \quad (30)$$

where $p = kx$, and p is a partial pressure (in atmospheres) of the gas in the vapor phase, calculated by subtracting the water vapor pressure given in the steam tables from the total pressure, and x is the mole fraction of gas in the solution. Within the experimental errors, this corresponds approximately to the Stephan *et al.* results, on which Eq. (30) is based.

3.7. Isotopic Fractionation during Solution

In column 6 of Table I the measured values for δ range from approximately 0.85 per mil ($\alpha = 1.00085$) at low temperatures to 0.55 per mil ($\alpha = 1.00055$) at 60 C. In Fig. 6, these results are plotted as $\ln \alpha (\times 10^3)$ vs. $1/T$, together with the data from Klots and Benson⁽³⁰⁾ and Kroopnick and Craig.^(3,4) Note that the ordinate in Fig. 6 is essentially equivalent to δ (expressed in per mil), because

$$\ln \alpha = \ln(1 + \delta) = \delta - \delta^2/2 + \delta^3/3 + \dots$$

Consequently, since $\delta < 0.001$ for oxygen, $\delta^2/2$ and higher-order terms are negligible, and to a very good approximation

$$\ln \alpha \div \delta$$

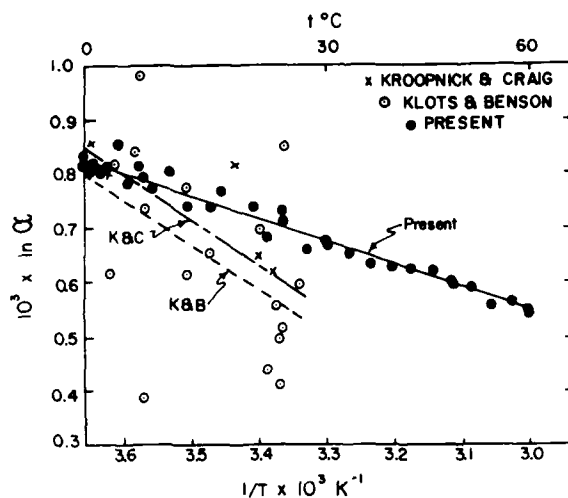


Fig. 6. Variation of the logarithm of the fractionation factor α for oxygen with the reciprocal of the absolute temperature. Results from previous work are also shown.

The high precision and relatively wide temperature range of the new measurements make possible an attempt to explore the variation of α with temperature. From Eqs. (19) and (24),

$$\begin{aligned}\ln \alpha &= \ln {}^{32}k - \ln {}^{34}k \\ &= ({}^{32}a_0 - {}^{34}a_0) + ({}^{32}a_1 - {}^{34}a_1)/T + ({}^{32}a_2 - {}^{34}a_2)/T^2\end{aligned}$$

or

$$\ln \alpha = \Delta a_0 + \Delta a_1/T + \Delta a_2/T^2 \quad (31)$$

which is similar in form to functions considered by Bigeleisen,⁽⁴⁷⁾ Bardo and Wolfsberg,⁽⁴⁸⁾ Rolston *et al.*,⁽⁴⁹⁾ van Hook and Phillips,⁽⁵⁰⁾ and others, in discussing isotope effects. Table VIII summarizes the results of fitting the data to various combinations of terms in Eq. (31). The standard deviation of $\ln \alpha$ for all forms is 0.017 per mil, which is comparable to the estimated precision of the measurements. Clearly, on the basis of these oxygen data alone, it is not possible to choose one of the functions as preferable. (Although the standard deviations are the same, the deviations at any specific temperature may differ slightly. The fit used in obtaining column 7 of Table I is the three-term fit, No. 1 in Table VIII.)

If desired, ${}^{34}k$ at any temperature may be calculated from

$$\ln {}^{34}k = 3.71937 + 5595.45/T - 1049624/T^2 \quad (32)$$

Table VIII. Fits of the Isotopic Fractionation Factor α to Functions of the Form $\ln \alpha = \Delta a_0 + \Delta a_1/T + \Delta a_2/T^2$, for Various Combinations of Terms

(1) $\ln \alpha =$	-0.0012263	$+ 0.72466/T$	$- 44.398/T^2$
(2) $\ln \alpha =$	-0.00072951	$+ 0.42696/T$	
(3) $\ln \alpha =$	-0.00001621		$+ 63.609/T^2$
(4) $\ln \alpha =$		$- 0.0092203/T$	$+ 64.914/T^2$
(5) $\ln \alpha =$			$62.223/T^2$

^a In all cases the standard deviation of both $\ln \alpha$ and δ is 0.017‰.

where the coefficients have been obtained from the relationships $^{34}a_i = ^{32}a_i - \Delta a_i$. (Again, the three-term function for $\ln \alpha$ has been used.)

If it is assumed that the isotopic fractionation is due to a difference in the zero-point energies of the two types of oxygen molecules in solution, then a calculation like that of Muccitelli and Wen⁽³⁴⁾ leads to a value of approximately 2.5 Å for the size of the solvent cage. For the solution of hydrogen, Muccitelli and Wen obtained approximately 3 Å. It might be argued that a smaller value should be expected for oxygen than for hydrogen, because the larger oxygen molecule would make the effective size of the cavity smaller, but additional precise measurements on other gases, and further theoretical studies of quantum effects in aqueous solutions, are needed before our understanding becomes more than qualitative.

It is evident that differences between $^{32}\text{O}_2$ and $^{34}\text{O}_2$ for the partial molal function changes may be calculated very simply from Eqs. (25) to (28) by substituting for a_0 , a_1 , and a_2 the coefficient differences Δa_0 , Δa_1 , and Δa_2 , respectively. For oxygen, of course, the difference in the change in heat capacity cannot be determined from the present data, because reference to the values for Δa_2 in Table VIII shows that the difference in $\Delta \bar{C}_p^\circ$ could be zero, negative, or positive, depending upon the function chosen for $\ln \alpha$. On the other hand, the values shown in Table IX for the other differences in thermodynamic changes are independent of the function chosen. The values for $(\Delta \bar{H}^\circ)/\Delta(\Delta \bar{H}^\circ)$ and $(\Delta \bar{S}^\circ)/\Delta(\Delta \bar{S}^\circ)$ are interesting because they indicate that substitution of an $^{34}\text{O}_2$ molecule for an $^{32}\text{O}_2$ molecule in solution involves a change in enthalpy with relatively little change in entropy.

4. CONCLUSION

A new method has been presented for determination of the Henry coefficient k and the isotopic fractionation factor α of gases dissolved in liquids. For oxygen the precision and probable accuracy of the measurements

Table IX. Differences at 298.15°K between $^{32}\text{O}_2$ and $^{34}\text{O}_2$ for the Partial Molal Thermodynamic Function Changes between the Usual Standard States

$\Delta(\Delta\bar{G}) = 0.418 \text{ cal-mole}^{-1}$	$\Delta\bar{G}^\circ/\Delta(\Delta\bar{G}^\circ) = 15,100$
$\Delta(\Delta\bar{H}) = 0.85 \text{ cal-mole}^{-1}$	$\Delta\bar{H}^\circ/\Delta(\Delta\bar{H}^\circ) = 3,400$
$\Delta(\Delta\bar{S}) = 0.0014 \text{ cal-}^\circ\text{K}^{-1}\text{-mole}^{-1}$	$\Delta\bar{S}^\circ/\Delta(\Delta\bar{S}^\circ) = 21,400$

$$^a \Delta(\Delta\bar{G}) = (\Delta\bar{G})_{32} - (\Delta\bar{G})_{34}, \text{ etc.}$$

of k are an order of magnitude better than previous results on any gas. This very high precision has shown that the best form for the variation of k with T , and perhaps for equilibrium constants of other systems, is the three-term power series in $1/T$ proposed by Benson and Krause. Their suggestion that the equation may be rewritten as a universal solubility equation is supported by the new oxygen results. The isotopic effects are small, but very precise analyses have provided the first quantitative determination of the variation of α with temperature for oxygen. Accurate values have been presented for the partial molal thermodynamic function changes between the liquid and vapor phases, including $\Delta\bar{C}_p$, which varies inversely with the square of the absolute temperature. The isotopic measurements on oxygen have shown that substitution of an $^{34}\text{O}_2$ molecule for an $^{32}\text{O}_2$ molecule in solution involves a change in enthalpy with a relatively small change in entropy. They are qualitatively consistent with the idea that the fractionation is the result of a difference of zero-point energy of the two molecules in solution. A new procedure has been suggested for calculating values for k at high temperatures until more precise measurements become available.

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k' vs. pressure was supported by Office of Naval Research Contract No. N00014-78-C-0198.

APPENDIX A

Although the equilibrator employed in the preliminary measurements reported by Benson and Krause ⁽²⁸⁾ is no longer used, a brief description of the experience with it should be reported because it suggests the possibility that solution of a gas in a very thin film of liquid may be influenced by the presence of the surface supporting the film.

A drawing of the unit is shown in Fig. A-1. It consisted essentially of an upper chamber A, a lower chamber B, and a connecting tube C. The total volume of the system was constant, but its distribution between A and B depended upon the position of the O-ring sealed piston. The piston and

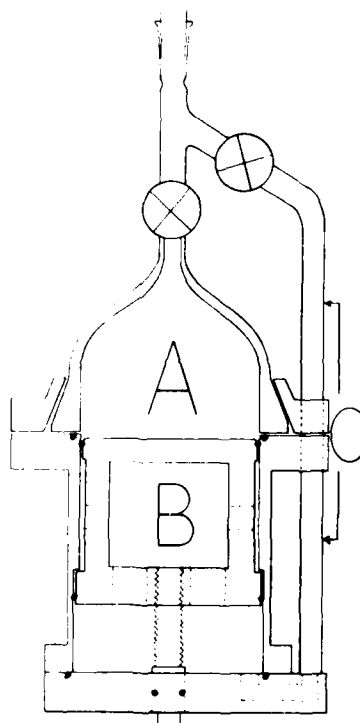


Fig. A-1. Drawing of the equilibrator used by Benson and Krause (ref. 28) for the preliminary measurements.

cylinder were made of Type 316 stainless steel. Two kinds of "heads" for chamber A were used. One was blown from 4-in.-diameter "Pyrex" pipe and included two 6 mm stopcocks at the top. The other was constructed of Type 316 stainless steel with specially designed stainless steel bellows valves. The O-rings were made of "Viton-A," and those in contact with the solution were ungreased.

With the piston in approximately the position shown, chamber A was filled with degassed water and then closed off. A vapor-phase sample bulb, with a stopcock and ground joint at each end, was attached to the top of the equilibrator, and the desired gas put into the bulb, tube C, and chamber B. The system was mounted vertically and fully immersed in a constant-temperature bath, the chambers were interconnected, and the piston drawn down almost to the bottom. The support frame for the equilibrator was tilted to approximately 45°, and the unit was set into rotation about its cylindrical axis to bring a continuously changing film of liquid along the wall of A into contact with the gas in essentially the same manner as that described by Green,⁽⁵¹⁾ who attributed the idea to Jacobsen.⁽⁵²⁾ After the desired interval of time, the vapor-phase sample bulb was closed to isolate a known volume of gas at the temperature of the bath. Then, in stages, the piston was raised and the tilt reduced, with rotation continued between adjustments, until the unit was upright and the lower flange of the piston was firmly against the shoulder stop on the cylinder. During this process the liquid level rose and displaced gas from A to B without trapping bubbles at the wall-liquid boundary and without pressure change within the system. With A closed off at the top, an accurately known volume of the solution was isolated. Subsequent gas extraction and drying procedures were similar to those described in Section 2.1.

After eliminating some initial problems with the groove design for the upper O-ring on the piston, the equilibrator gave very precise results which permitted detection of relatively small, but significant, systematic effects apparently associated with the thin film. Summarized briefly, the following characteristics were observed:

- (1) At all the rotation speeds that were employed, the kinetics of equilibration were determined by the rate of formation of film on the wall of A.
- (2) In the early measurements the kinetics for a given speed of rotation seemed to follow the Adeney-Becker⁽⁵³⁾ growth curve (attributed to Carlson⁽⁵⁴⁾ by Montgomery *et al.*⁽¹⁷⁾). Later, however, semilog plots for long equilibration periods revealed a dual half-time. Typically, for example, at low temperatures an initial half-time of 15 min shifted to a half-time of 5 h when the water became nearly saturated.

This seemed to imply a different control mechanism near the end of the process.

- (3) As the temperature was increased, the rate of equilibration decreased markedly. This is consistent with the very large decrease in the viscosity of water at high temperatures, which would lead to much thinner films on the surface and reduce mixing in the bulk of the liquid.
- (4) Approach to equilibrium from both the undersaturated and supersaturated states showed that, near equilibrium, the same concentration was reached from both initial states, but that the common value for the concentration increased and approached the equilibrium value with the longer half-time. It is clear that this traditional test for equilibrium is not conclusive unless the pairs of measurements are shown to give the same results for several different equilibration periods. Later, after results were available from the equilibrator described in Section 2.1, it became evident that, in the very long equilibration periods, the thin-film equilibrator could yield solutions apparently slightly supersaturated relative to the bulk liquid.
- (5) The value of k depended upon whether the liquid film was in contact with a stainless steel wall or a glass wall in chamber A. For example, with both oxygen and argon at 2°C, k was greater by approximately 0.1% with stainless steel.
- (6) Tests showed that these effects were not caused by contamination from either real or virtual vacuum leaks, by incomplete mixing in chamber A, or by vacuum grease in the stopcock at the top of chamber A in the glass head.

After the equilibrator in Fig. 1 proved to give excellent results without any of the above problems, no further attempts were made to pursue the source of the difficulties. The observations are consistent, however, with the hypothesis that the properties of a thin film clinging to a wall of metal or glass may be different from those of the bulk liquid. Adsorption of gas on the large surface area of chamber A may also have played a role, because chamber A served the dual function of equilibration vessel and liquid-phase sample bulb. Note that the walls of the liquid-phase sample bulb in Fig. 1 are exposed only to the liquid phase.

Prior to the preliminary measurements reported in 1976, initial tests were conducted to estimate appropriate equilibration periods. In carrying them out it was assumed that the longest times would be required at low temperatures because of the higher equilibrium concentrations and the (presumably) slower kinetics of exchange and mixing. After 20 h seemed to be roughly satisfactory at low temperatures, that period was used for most of the pre-

liminary measurements. The results for oxygen were that near 0°C the solution was nearly saturated (k was only 0.11% high), but as the temperature was raised the solution became systematically more undersaturated so that k was 0.76% high at 35°C. Despite this systematic error, the primary conclusions from the preliminary work, i.e., the functional dependence of k on T and the relationships between solution and molecular parameters, remain valid.

APPENDIX B

For comparison, the notation here follows Clarke and Glew.⁽²³⁾ At any given temperature the equilibrium constant is related to the standard thermodynamic function changes by

$$R \ln K_p = -\frac{\Delta G_T^\circ}{T} = \Delta S_T^\circ - \frac{\Delta H_T^\circ}{T} \quad (\text{B-1})$$

where ΔG_T° , ΔS_T° , and ΔH_T° are functions of temperature only. If we now assume that the standard thermodynamic-function changes are well behaved functions of the reciprocal of the absolute temperature $1/T$, then ΔH_T° can be expanded in a Taylor series about the reference reciprocal temperature $1/\theta$. Then defining

$$\beta \equiv \frac{1}{T} - \frac{1}{\theta} \quad (\text{B-2})$$

so that $\beta = 0$ when $T = \theta$, and also denoting the derivatives evaluated at $T = \theta$ by

$$D_i \equiv \left[\frac{d^i \Delta H_T^\circ}{d\beta^i} \right]_{\beta=0}$$

we have the Taylor expansion

$$\Delta H_T^\circ = \Delta H_\theta^\circ + D_1\beta + \frac{1}{2}D_2\beta^2 + \dots \quad (\text{B-3})$$

We also have the relations

$$\Delta H_T^\circ = -T^2 \left[\frac{\partial(\Delta G_T^\circ/T)}{\partial T} \right]_p \quad (\text{B-4})$$

$$\Delta S_T^\circ = - \left[\frac{\partial(\Delta G_T^\circ)}{\partial T} \right]_p \quad (\text{B-5})$$

and

$$\Delta C_{pT}^\circ = \left[\frac{\partial(\Delta H_T^\circ)}{\partial T} \right]_p \quad (\text{B-6})$$

so that

$$\Delta C_{pT}^{\circ} = [-D_1 + D_2(1/\theta) + \dots]/T^2 + [-D_2 + \dots]/T^3 + \dots \quad (\text{B-7})$$

Using the relation between ΔS_T° and ΔC_{pT}° , we have

$$\Delta S_T^{\circ} = \Delta S_0^{\circ} + \int_{\theta=0}^{\theta} \frac{\Delta C_{pT}^{\circ}}{T} dT \quad (\text{B-8})$$

and then combining Eqs. (B-7) and (B-8) with (B-1) and (B-3), we have

$$\begin{aligned} R \ln K_p = & \left[\Delta S_0^{\circ} + \frac{D_1}{2\theta^2} - \frac{D_2}{6\theta^3} + \dots \right] + \left[-\Delta H_0^{\circ} + \frac{D_1}{\theta} - \frac{D_2}{\theta^2} + \dots \right] \frac{1}{T} \\ & + \left[-\frac{3D_1}{2} + \frac{3D_2}{2\theta} + \dots \right] \frac{1}{T^2} + \left[-\frac{5D_2}{6} + \dots \right] \frac{1}{T^3} + \dots \quad (\text{B-9}) \end{aligned}$$

This may be rewritten as

$$R \ln K_p = a_0 + a_1/T + a_2/T^2 + a_3/T^3 + \dots \quad (\text{B-10})$$

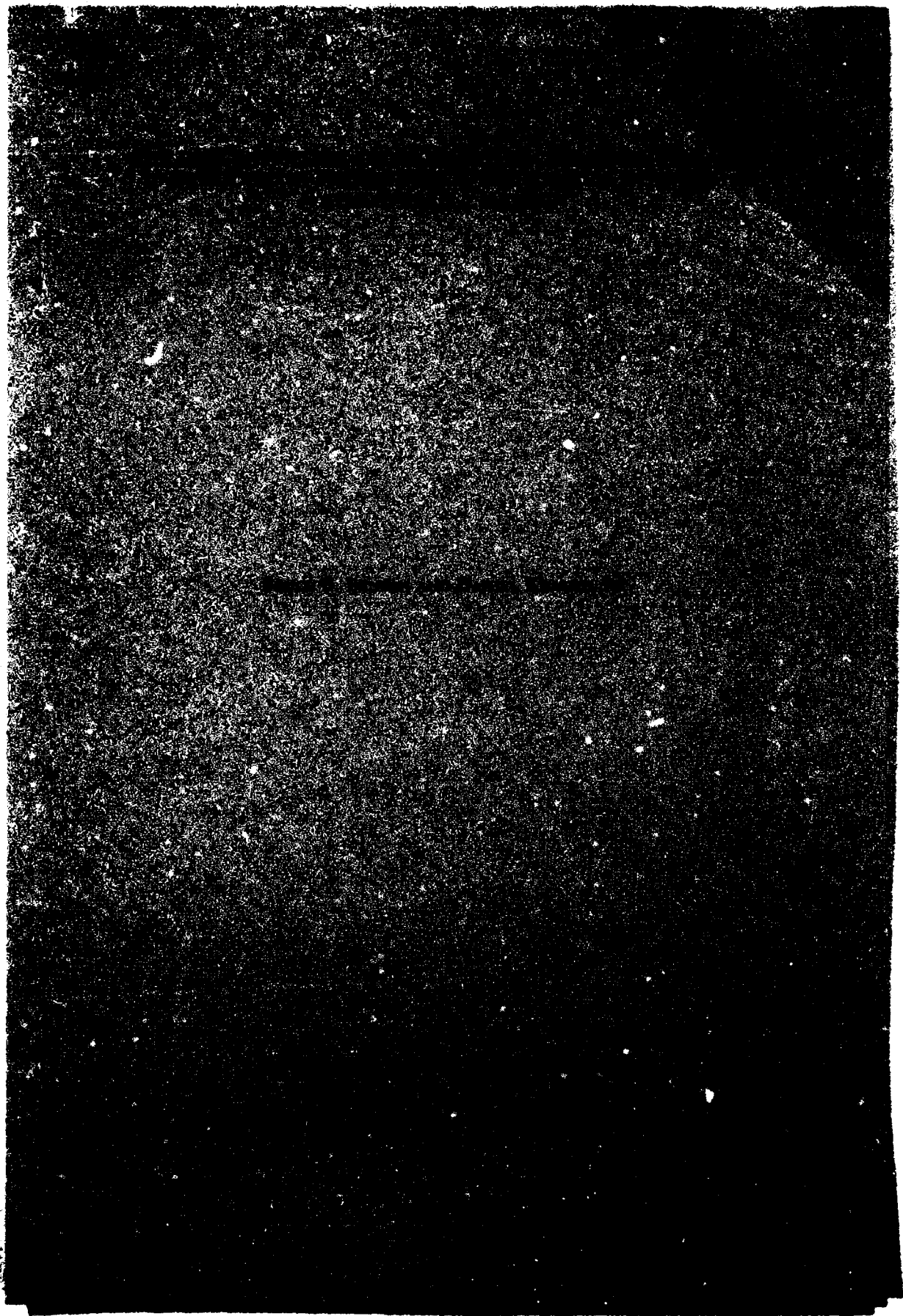
which corresponds to Eq. (2). From Eqs. (B-1), (B-4), (B-5), (B-6), and (B-10) it is evident that the thermodynamic-function changes ΔG_T° , ΔH_T° , ΔS_T° , and ΔC_{pT}° are very simply related to the coefficients obtained from fitting the experimental data to Eq. (B-10) for the temperature dependence of equilibrium constants.

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² Pages 44 to 47 present an excellent discussion of how to operate with the systems associated with the Clarke and Glew analysis.



The concentration and isotopic fractionation of gases dissolved in freshwater in equilibrium with the atmosphere. 1. Oxygen

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Abstract

Equations and tables are presented from which accurate values can be obtained, in any of several sets of units, for the concentration of oxygen dissolved in freshwater in equilibrium with the atmosphere from 0° to 40°C and 0.5 to 1.1 atm. They are based on values for the Henry coefficient of oxygen, k_H , which have an estimated accuracy of 0.02%. Equations are derived which relate k_H to equilibrium concentrations in natural waters. The equations include corrections for molecular interactions in the vapor phase. Uncertainty about the best way to correct for these interactions limits the estimated accuracy of the derived values to about $\pm 0.07\%$ at 0°C and 0.04% at 40°C, but the new results are much more accurate than values from the UNESCO tables. Within their random errors, previous measurements agree very well with the new results. Under equilibrium conditions, and between 0° and 60°C, the per mil difference between the $^{34}\text{O}_2$: $^{32}\text{O}_2$ abundance ratio in the dissolved gas and the air is given by $\delta = -0.730 + (427/T)$, where T is in kelvin and the standard deviation is $<0.02\%$.

Accurate values for the solubility of oxygen are necessary to interpret dissolved oxygen concentrations in natural waters. For many years, values based on the measurements of Winkler (1889, 1891) and Fox (1909) were used as standards. After the determinations of Truesdale et al. (1955) raised doubts about the Winkler and Fox standards, new measurements were undertaken by many workers. Klotz and Benson (1963a), Montgomery et al. (1964), Carpenter (1966), and Murray and Riley (1969), using different methods, obtained agreement within the scatter of their data, i.e. about $\pm 0.2\%$, for the solubility of oxygen in pure water over the range 0°–35°C. Until recently these have constituted the most accurate solubility data available for any gas.

Results from solubility measurements have been smoothed in many different ways, by graphical and analytical methods and combinations of the two (see Benson and Krause 1976). Valentiner (1927) assumed that the change in partial molal heat capacity of a gas during solution was independent of temperature and derived from the van't Hoff equation the expression

$$\ln L = A_0 + (A_1/T) + A_2 \ln T \quad (1)$$

for the variation of the Ostwald coefficient

with temperature. (Throughout this paper we shall use T for kelvin temperatures and t for Celsius temperatures.)

Clarke and Glew (1966) presented a systematic treatment of the generalized Valentiner function

$$\ln k = A_0 + (A_1/T) + A_2 \ln T + A_3 T + A_4 T^2 + \dots \quad (2)$$

for equilibrium constants in general. Weiss (1970) used the oxygen data of Carpenter (1966) and Murray and Riley (1969) for both pure water and seawater to fit series of this form in temperature, with additional terms for the effect of salinity, to Bunsen coefficients and various concentration values. Postma et al. (1976) used the Weiss results to calculate oxygen solubilities vs. temperature and salinity in the UNESCO *International Oceanographic Tables*, Vol. 2. We (Benson and Krause 1976) have proposed

$$\ln k = a_0 + (a_1/T) + (a_2/T^2) + (a_3/T^3) + \dots \quad (3)$$

for the temperature dependence of the Henry coefficient of gases dissolved in pure water, and we found that use of the three-term version of this expression reveals relationships between the molecular properties of gases and the thermodynamic properties of their solutions.

Benson et al. (1979) have obtained very

precise and accurate new experimental results for the Henry coefficient of oxygen in pure water from 0° to 60°C. The random error in these measurements is about 0.02%, which is an order of magnitude lower than in previous work. Agreement within the random errors in the earlier studies, and extensive tests, indicate that the new measurements probably are free from systematic errors and that the accuracy is limited by the precision. The new oxygen data show that Eq. 3 provides a much better representation of the variation of k with T than the generalized Valentiner function or any other function that has been considered. For 37 data points only a three-term power series in $1/T$ is required to give a precision of fit that is better than 0.02% for the full 60°C temperature range. Furthermore, Benson et al. have shown that Eq. 3 follows from a systematic thermodynamic analysis that is equivalent to the Clarke and Glew (1966) treatment of the generalized Valentiner function.

Our purpose in this paper is to derive from these new results very accurate values for the various quantities commonly used to specify equilibrium concentrations of oxygen in freshwater from 0° to 40°C. Equations and tables are presented which constitute significant improvements over the UNESCO tables. In addition, we express the results of our measurements of the isotopic fractionation of oxygen during solution in a form most useful for geochemical studies.

We have benefited from many discussions of solubility problems with D. E. Carritt and J. H. Carpenter. We thank D. E. Carritt and R. Battino for reading the manuscript critically. Comments from C. H. Mortimer and R. F. Weiss have been very useful. This work was supported in part by National Science Foundation grant OCE 78-08120 and in part by Office of Naval Research contract N00014-78-C-0198.

Equilibrium concentration and the Henry coefficient

Henry's law states that $f_i = k_i x_i$, where f_i is the fugacity of the i th gas in the vapor

phase and x_i is its mole fraction in the liquid phase. Although the Henry coefficient k_i is more fundamental because of its direct relationship to the changes in the chemical potential and the other partial molal thermodynamic functions, other ways of expressing gas solubilities are more useful for studies of natural waters.

Suppose that a body of pure water is in thermodynamic equilibrium with an atmosphere of standard composition saturated with water vapor at a total pressure P . For oxygen we may write Henry's law as

$$f_o = k_o \frac{n_{od}}{n_w + n_{od} + n_{Rd}} \quad (4)$$

where n_w and n_{od} are the numbers of moles of water and of dissolved oxygen in some volume V_s of solution, and n_{Rd} is the number of moles of all other dissolved gases, i.e. essentially nitrogen. If \bar{v}_o and \bar{v}_R are the partial molal volumes of oxygen and of the residual gas, and M and ρ are the gram molecular mass and density of pure water, the volume V_s at the temperature of equilibrium is given by

$$V_s = \frac{M}{\rho} \left[n_w + (\bar{v}_o n_{od} + \bar{v}_R n_{Rd}) \frac{\rho}{M} \right] \quad (5)$$

Then, solving for n_{od} in the numerator of Eq. 4, dividing the result by V_s , and substituting Eq. 5, we obtain the expression

$$C_o = \frac{n_{od}}{V_s} = \frac{f_o \rho}{k_o M} \left[\frac{n_w + n_{od} + n_{Rd}}{n_w + (\bar{v}_o n_{od} + \bar{v}_R n_{Rd}) \frac{\rho}{M}} \right] \quad (6)$$

for the equilibrium concentration of dissolved oxygen in moles of oxygen per volume of solution. If we assume that the Lewis and Randall rule applies to this system,

$$f_o = x_o f_o^* \quad (7)$$

where f_o^* is the fugacity pure oxygen would have at the equilibrium temperature if its pressure were the same as the total pressure P of the mixed vapor phase.

Benson et al. (1979) showed that

$$f'_0 = PZ'_0 \quad (8)$$

where Z'_0 is the compressibility factor for pure oxygen at the equilibrium temperature and the total pressure P . [Benson et al. referred to f'_0 and Z'_0 as f^* and Z^* (and P as P_t). The notation is changed here because, following geochemical custom, the asterisk is used in conjunction with C_0 to denote something quite different.] Furthermore, by definition,

$$P_0 = x_0 P. \quad (9)$$

If Eq. 7, 8, and 9 are combined, and $(1 - \theta_0 P)$ is substituted for Z'_0 , the result is

$$f_0 = P_0(1 - \theta_0 P) \quad (10)$$

where θ_0 is the negative of the second pressure coefficient in the virial expansion for the real gas behavior of oxygen. The argument leading to Eq. 10 is essentially equivalent to assuming that for a mixture of real gases, the virial cross-term B_{ij} is equal to $(B_{ii} + B_{jj})/2$, where the second virial coefficient B_{ij} takes account of interactions between pairs of molecules of type i , B_{jj} between pairs of type j , and B_{ij} between mixed pairs of molecules (e.g. see Guggenheim 1950, Sect. 5.14 and 6.14).

When Eq. 10 is inserted into Eq. 6, and it is recognized that the ratio in the brackets in Eq. 6 differs from unity by only 20 or 30 ppm (see Enns et al. 1965 for values of the partial molal volumes), the result is

$$C_0 = \frac{n_{0d}}{V_s} = \frac{\rho P_0}{k_0 M} (1 - \theta_0 P). \quad (11)$$

Therefore, at any P_0 and P the concentration of dissolved oxygen can be calculated from values for k_0 , θ_0 , and ρ . From Benson et al., k_0 is given by

$$\ln k_0 = 3.71814 + (5596.17/T) - (1.049,668/T^2) \quad (12)$$

where T is in kelvin and k_0 in atm, and for $0^\circ < t < 40^\circ\text{C}$,

$$\theta_0 = 0.000975 - (1.426 \times 10^{-5}t) + (6.436 \times 10^{-8}t^2). \quad (13)$$

(Equation 13 is eq. 10 in Benson et al., which is based on second virial coefficients given by Sengers et al. 1972.) Furthermore, we have found that over the range 0° – 40°C the density of water in $\text{g}\cdot\text{cm}^{-3}$ can be calculated from

$$\ln \rho = -0.589581 + (326.785/T) - (45,284.1/T^2) \quad (14)$$

with an error no larger than 20 ppm. Again, T is in kelvin.

It should be noted that Eq. 11 is not restricted to the equilibrium of air with water. Within the stated assumptions it is valid for any mixture including pure oxygen.

The Bunsen coefficient

A Bunsen coefficient for oxygen, β_0 , may be defined as the number of moles of dissolved oxygen (or, equivalently, the volume the dissolved oxygen would occupy at STP if it were an ideal gas) per unit volume of solution per unit partial pressure of oxygen above the solution. Various workers have defined Bunsen coefficients in other ways, but this formulation is most useful for geochemical work. From this definition and Eq. 11,

$$\beta_0 \equiv \frac{n_{0d}}{V_s P_0} = \frac{\rho}{k_0 M} (1 - \theta_0 P). \quad (15)$$

This shows that β_0 depends upon not only the temperature through k_0 , ρ , and θ_0 , but also the total pressure P . Usually, the Bunsen coefficient is referred to a situation in which pure oxygen with a partial pressure of 1 atm is above the solution, but Eq. 15 implies that the same result would be obtained with 1 atm pressure of air. Then, denoting this Bunsen coefficient by β'_0 ,

$$\beta'_0 = \frac{\rho}{k_0 M} [1 - \theta_0(1 + P_{wr})], \quad (16)$$

where P_{wr} is the saturated vapor pressure of water in atmospheres at the temperature of equilibrium.

Because the present discussion is limited to temperatures below 40°C , the quantity $\theta_0 P_{wr}$ can be neglected. (Even at 40°C , it is ~ 0.00004 .) Eq. 16 then reduces to

$$\beta^1_o = \frac{\rho}{k_o M} (1 - \theta_o). \quad (17)$$

Although the remaining factor $(1 - \theta_o)$ differs only slightly from unity (it varies from 0.99902 at 0°C to 0.99949 at 40°C), for accurate values of β^1_o it must be included to correct for molecular interactions in the vapor phase. Substituting $M = 18.0153 \text{ g} \cdot \text{mol}^{-1}$ in Eq. 17 gives

$$\beta^1_o = 5.5508 \times 10^7 \frac{\rho}{k_o} (1 - \theta_o) \quad (18)$$

where β^1_o is in $\mu\text{mol} \cdot \text{dm}^{-3}$ of solution per atm when ρ , the density of pure water, is in $\text{g} \cdot \text{cm}^{-3}$ and k_o is in atm. For β^1_o in cm^3 of ideal gas at STP $\cdot \text{dm}^{-3} \cdot \text{atm}^{-1}$, we replace the numerical coefficient in Eq. 18 with 1.24416×10^6 . (The volume of 1 mole of ideal gas at STP has been taken to be $22,414 \text{ cm}^3$.)

To facilitate the determination of values for β^1_o , we have fitted the logarithms of values calculated from Eq. 18 (with the aid of Eq. 12-14) to a three-term power series in the reciprocal of the absolute temperature. The result is

$$\ln \beta^1_o = 13.5246 - (5.26895 \times 10^3/T) + (1.00417 \times 10^6/T^2) \quad (19)$$

where β^1_o is in $\mu\text{mol} \cdot \text{dm}^{-3} \cdot \text{atm}^{-1}$. For values in cm^3 of ideal gas at STP $\cdot \text{dm}^{-3} \cdot \text{atm}^{-1}$, we substitute 9.7265 for the first constant. Over the range 0°–40°C, values determined from Eq. 19 differ from those obtained from Eq. 18 by less than the uncertainty in k_o . The excellent fit of $\ln \beta^1_o$ to the three-term series in $1/T$ is not surprising, because ρ and $(1 - \theta_o)$ vary only slightly with temperature.

Equilibrium concentrations from a unit standard atmosphere

For oxygen, the unit standard atmospheric concentration by volume, C^*_o , or, more briefly, the unit standard concentration, is defined here as the concentration of dissolved oxygen per unit volume of solution (measured at equilibrium temperature) when it is in equilibrium with an atmosphere of standard composition and saturated with water vapor, at a total pressure (including that of the water va-

por) of 1 atm. In the past solubility, equilibrium solubility, and sometimes air solubility have been used for this concept. The first, however, also is commonly used to refer in a general collective sense to the solution process and ways of describing it. Neither solubility nor equilibrium solubility suggests that the system is composed of the solution and the atmosphere, while air solubility literally implies a concentration of air. Although no procedure, short of creating a new word, is ideal for both clarity and brevity, choice of unit standard concentration offers the advantages of indicating that it is a *concentration* under standard conditions, i.e. equilibrium with a *standard atmosphere* at unit pressure. The unit standard concentration by mass, C^\dagger_o , is defined in an analogous way, except that the concentration is referred to unit *mass* of solution. If both C^*_o and C^\dagger_o are referred to as unit standard concentrations, the asterisk and dagger, and the associated units, will distinguish between them.

In order to write down an expression for C^*_o from Eq. 11, we need an expression for P_o . For temperatures below 40°C the saturated vapor pressure of pure water is <0.08 atm. Consequently, the common practice of taking the difference between the total pressure $P = 1$ atm and the value for P_{wr} read from the steam tables (in atm) probably yields a good approximation for the partial pressure of the remaining gases. Then, again using the definition that the partial pressure of a gas in a mixture is equal to its mole fraction times the pressure of the mixture, we have

$$P_o = 0.20946(1 - P_{wr}), \quad (20)$$

and

$$C^*_o = 0.20946(1 - P_{wr}) \frac{\rho}{k_o M} (1 - \theta_o), \quad (21)$$

or, in terms of β^1_o from Eq. 17,

$$C^*_o = 0.20946(1 - P_{wr}) \beta^1_o. \quad (22)$$

The value 0.20946 for the mole fraction of oxygen in dry air is from Glueckauf

(1951). For convenience in calculating C^*_o , we have expressed the temperature dependence of P_{wr} by

$$\ln P_{wr} = 11.8571 - (3,840.70/T) - (216,961/T^2) \quad (23)$$

where T is in kelvin and P_{wr} is in atm. Between 0° and 40°C Eq. 23 gives values for $(1 - P_{wr})$ that differ from the standard values by only 11 ppm rms. Using k_o , θ_o , ρ , and P_{wr} from Eq. 12, 13, 14, and 23, we have calculated values for C^*_o from Eq. 21 at integral temperatures. These are given in Table 1 in three sets of units: $\mu\text{g-atoms}\cdot\text{dm}^{-3}$, cm^3 (ideal gas at STP) $\cdot\text{dm}^{-3}$, and $\text{mg}\cdot\text{dm}^{-3}$. [To conform with the International Association of Physical Oceanographers (Helland-Hansen et al. 1948) and the Joint Panel on Oceanographic Tables and Standards (Postma et al. 1976) we have expressed the first set in $\mu\text{g-atoms}$ rather than μmol . For the last set 1 mole of oxygen has been taken to be 31.9988 g.]

To obtain C^\dagger_o , it is necessary only to divide C^*_o by the density of the solution. To an excellent approximation, however, the latter is equal to ρ , the density of pure water. Therefore, from Eq. 21,

$$\begin{aligned} C^\dagger_o &= \frac{C^*_o}{\rho} \\ &= 0.20946(1 - P_{wr}) \frac{1}{k_o M} (1 - \theta_o P). \end{aligned} \quad (24)$$

Values for C^\dagger_o have been calculated at integral temperatures from Eq. 24. They are shown in the last three columns of Table 1 in $\mu\text{g-atoms}\cdot\text{kg}^{-1}$, cm^3 (ideal gas at STP) $\cdot\text{kg}^{-1}$, and $\text{mg}\cdot\text{kg}^{-1}$.

For use in either fieldwork or the laboratory Table 1 provides a simple means for finding very accurate values for C^*_o and C^\dagger_o . Linear interpolation between degrees introduces an error not >0.017%. For computer application we have fitted both $\ln C^*_o$ and $\ln C^\dagger_o$, calculated as above, to power series in the reciprocal of the kelvin temperature. Although, as we have seen, $\ln \beta^1_o$ fits a three-term function extraordinarily well, more terms are required for C^*_o and C^\dagger_o because $(1 - P_{wr})$

has a different functional form from β^1_o . The standard deviations for three-, four-, and five-term series are 0.16, 0.026, and 0.004%. The two five-term series are the briefest within the precision of the Benson et al. (1979) values for k_o . For C^*_o in $\mu\text{g-atoms}\cdot\text{dm}^{-3}$,

$$\begin{aligned} \ln C^*_o &= -135.20890 \\ &+ (1.575701 \times 10^5/T) \\ &- (6.642308 \times 10^7/T^2) \\ &+ (1.243800 \times 10^{10}/T^3) \\ &- (8.621949 \times 10^{11}/T^4). \end{aligned} \quad (25)$$

To obtain C^*_o in $\text{cm}^3\cdot\text{dm}^{-3}$ or $\text{mg}\cdot\text{dm}^{-3}$, we replace the first constant in Eq. 25 with -139.70011 or -139.34410 . Similarly, for C^\dagger_o in $\mu\text{g-atoms}\cdot\text{kg}^{-1}$,

$$\begin{aligned} \ln C^\dagger_o &= -134.60690 \\ &+ (1.572288 \times 10^5/T) \\ &- (6.637149 \times 10^7/T^2) \\ &+ (1.243678 \times 10^{10}/T^3) \\ &- (8.621061 \times 10^{11}/T^4), \end{aligned} \quad (26)$$

and when C^\dagger_o is desired in $\text{cm}^3\cdot\text{kg}^{-1}$ or $\text{mg}\cdot\text{kg}^{-1}$, we substitute -139.09811 or -138.74210 for the first constant in Eq. 26.

Equilibrium concentrations vs. atmospheric pressure

It is useful to have a simple way of calculating the equilibrium concentration of dissolved oxygen in a situation where the atmospheric pressure is different from unity. The more general form of Eq. 21,

$$C^p_o = 0.20946(P - P_{wr}) \frac{\rho}{k_o M} (1 - \theta_o P), \quad (27)$$

is the appropriate equation to use (if we assume that the composition of the atmosphere is uniform), but to use it in the field would be cumbersome. However,

$$C^p_o = C^*_o P \left[\frac{(1 - P_{wr}/P)(1 - \theta_o P)}{(1 - P_{wr})(1 - \theta_o)} \right]. \quad (28)$$

Values for the quantity in brackets for oxygen are given in Table 2 for pressures from 1.1 to 0.5 atm (the latter corresponds to an altitude of about 5 km), and for temperatures from 0° to 40°C. Accurate val-

Table 1. Values for C^*_{O} and C^*_{O} in various sets of units at integral temperatures. Linear interpolation between degrees will introduce an error $\pm 0.017\%$. To convert from $\mu\text{g-atoms}$ to μmol divide by 2.

Temp C	C^*_{O}			C^*_{O}		
	$\frac{\mu\text{g-atoms}}{\text{dm}^3}$	$\frac{\text{cm}^3}{\text{dm}^3}$	$\frac{\text{mg}}{\text{dm}^3}$	$\frac{\mu\text{g-atoms}}{\text{kg}}$	$\frac{\text{cm}^3}{\text{kg}}$	$\frac{\text{mg}}{\text{kg}}$
0.0	913.85	10.2415	14.6211	913.99	10.2432	14.6235
1.0	888.53	9.9577	14.2160	888.62	9.9588	14.2174
2.0	864.36	9.6869	13.8293	864.41	9.6875	13.8302
3.0	841.28	9.4282	13.4600	841.31	9.4286	13.4606
4.0	819.23	9.1811	13.1072	819.26	9.1814	13.1077
5.0	798.15	8.9448	12.7699	798.18	8.9452	12.7705
6.0	777.98	8.7188	12.4473	778.03	8.7194	12.4481
7.0	758.68	8.5025	12.1385	758.75	8.5034	12.1397
8.0	740.19	8.2954	11.8427	740.31	8.2966	11.8445
9.0	722.48	8.0969	11.5593	722.64	8.0986	11.5619
10.0	705.50	7.9065	11.2876	705.71	7.9089	11.2910
11.0	689.21	7.7240	11.0270	689.48	7.7270	11.0313
12.0	673.57	7.5487	10.7768	673.91	7.5525	10.7822
13.0	658.56	7.3805	10.5366	658.96	7.3850	10.5431
14.0	644.13	7.2187	10.3057	644.61	7.2242	10.3134
15.0	630.25	7.0633	10.0837	630.82	7.0696	10.0927
16.0	616.91	6.9137	9.8702	617.55	6.9210	9.8806
17.0	604.06	6.7697	9.6647	604.80	6.7780	9.6764
18.0	591.69	6.6311	9.4667	592.51	6.6403	9.4799
19.0	579.76	6.4974	9.2759	580.68	6.5078	9.2907
20.0	568.27	6.3686	9.0920	569.28	6.3800	9.1083
21.0	557.17	6.2443	8.9145	558.29	6.2568	8.9324
22.0	546.46	6.1242	8.7431	547.68	6.1379	8.7626
23.0	536.12	6.0083	8.5776	537.44	6.0231	8.5987
24.0	526.11	5.8962	8.4176	527.54	5.9122	8.4404
25.0	516.44	5.7878	8.2628	517.97	5.8049	8.2873
26.0	507.08	5.6828	8.1130	508.71	5.7012	8.1392
27.0	498.01	5.5812	7.9679	499.75	5.6007	7.9958
28.0	489.22	5.4827	7.8272	491.07	5.5034	7.8569
29.0	480.69	5.3871	7.6908	482.65	5.4091	7.7222
30.0	472.42	5.2944	7.5584	474.49	5.3176	7.5915
31.0	464.38	5.2043	7.4298	466.56	5.2287	7.4647
32.0	456.56	5.1167	7.3048	458.85	5.1424	7.3414
33.0	448.96	5.0315	7.1831	451.36	5.0584	7.2215
34.0	441.56	4.9486	7.0647	444.06	4.9767	7.1048
35.0	434.35	4.8677	6.9493	436.96	4.8970	6.9912
36.0	427.31	4.7889	6.8368	430.04	4.8194	6.8803
37.0	420.45	4.7120	6.7269	423.28	4.7437	6.7722
38.0	413.74	4.6368	6.6196	416.68	4.6697	6.6666
39.0	407.18	4.5633	6.5147	410.22	4.5974	6.5634
40.0	400.76	4.4913	6.4119	403.91	4.5266	6.4623

ues for C^*_{O} can be obtained by simply multiplying C^*_{O} from either Table 1 or Eq. 25, by the product of P and the appropriate value for the bracket from Table 2.

Linear interpolation in P and t will introduce an error $\pm 0.02\%$ in the upper and left sections of Table 2. Interpolations from numbers in parentheses will lead to errors $\pm 0.05\%$. With the numbers in brackets, the interpolation errors rapidly

become larger, but this region for P and t is not usually of interest in geochemical studies. It is obvious that Eq. 28 and the procedure just described are equally applicable to C^*_{O} .

Isotopic fractionation of atmospheric oxygen during solution

From direct mass spectrometric comparison of the $^{34}\text{O}_2$: $^{32}\text{O}_2$ abundance ratio in the dissolved gas with the correspond-

Table 2. Values for quantity bracketed in Eq. 28 vs. P and t . Linear interpolation in P and t will introduce an error $< 0.02\%$ in upper and left sections of table. Interpolations using numbers in parentheses will lead to errors $< 0.05\%$. With the numbers in brackets, interpolation errors become larger. Either temperature or pressure may be interpolated first, as illustrated for $t = 3.00^\circ\text{C}$ and $P = 0.67$ atm by the two arrays below the body of the table.

t °C	P , atm						
	1.1	1.0	0.9	0.8	0.7	0.6	0.5
0.0	1.0005	1.0000	0.9994	0.9987	0.9977	0.9963	0.9944
5.0	1.0007	1.0000	0.9991	0.9980	0.9966	0.9946	0.9918
10.0	1.0010	1.0000	0.9987	0.9971	0.9950	0.9922	0.9882
15.0	1.0015	1.0000	0.9982	0.9959	0.9929	(0.9889)	(0.9833)
20.0	1.0021	1.0000	0.9974	0.9942	(0.9901)	(0.9845)	[0.9767]
25.0	1.0029	1.0000	0.9965	0.9921	(0.9864)	(0.9787)	[0.9680]
30.0	1.0039	1.0000	0.9952	(0.9892)	(0.9814)	[0.9711]	[0.9566]
35.0	1.0053	1.0000	(0.9935)	(0.9854)	(0.9750)	[0.9610]	[0.9415]
40.0	1.0071	1.0000	(0.9913)	(0.9805)	[0.9665]	[0.9479]	[0.9217]

Temp first				Press. first			
	0.7	0.67	0.6		0.7	0.67	0.6
0	0.9977		0.9963	0	0.9977	0.99728	0.9963
3	0.99704	0.9965	0.99528	3		0.9965	
5	0.9966		0.9946	5	0.9966	0.99600	0.9946

ing ratio in the gas above the solution, Benson et al. (1979) confirmed the earlier observations by Klotz and Benson (1963b) on oxygen in pure water, and by Kroopnick and Craig (1972) on oxygen in seawater, that at equilibrium the heavier molecule is slightly more soluble. In addition, however, the higher precision and the wider temperature range of the new measurements provide quantitative information about the variation of the oxygen isotope fractionation with temperature. These results are directly applicable to atmospheric oxygen, because the presence of the other gases should not influence the fractionation significantly, but for geochemical purposes the most useful way to express the fractionation as a function of temperature is

$$\delta = -0.730 + (427/T) \quad (29)$$

where T is in kelvin, and δ is the per mil difference between the $^{34}\text{O}_2$: $^{32}\text{O}_2$ abundance ratio in the dissolved gas and the $^{34}\text{O}_2$: $^{32}\text{O}_2$ ratio in atmospheric oxygen when freshwater is in equilibrium with air.

We emphasize that Eq. 29 will give the isotopic difference between dissolved and atmospheric oxygen under *equilib-*

rium conditions only. In addition to biological and chemical activity, physical kinetic effects can influence the isotopic ratio in the dissolved gas. For example, during our preliminary measurements (Benson and Krause 1976), we determined the isotopic ratio in the dissolved gas as a function of the interval after the degassed water was brought into contact with the gas. Initially, as a result of the faster kinetics of the lighter molecule, the $^{34}\text{O}_2$: $^{32}\text{O}_2$ ratio in the dissolved gas was found to be lower than in the gas above the solution, but as time progressed the dissolved ratio increased, then surpassed that of the gas above, and finally stabilized at the higher equilibrium value.

Discussion

The empirical method described by Benson et al. (1979) determines k directly. It yields fully corrected values for k without the necessity of making theoretical assumptions about how to take care of molecular interactions in the vapor phase. Similarly, the methods used by Montgomery et al. (1964), Carpenter (1966), and Murray and Riley (1969) determine C^* directly. To calculate C^* from k , or vice versa, however, it is necessary

to include virial corrections if the data are sufficiently accurate. In the absence of experimental information about cross-interactions in gas mixtures, we have invoked the Lewis and Randall rule and assumed the applicability of the definition of partial pressure which is implicit in the expressions $P_0 = x_0 P$ and $P_0 = 0.20946(P - P_{\text{air}})$. Other theoretical possibilities exist. For example, in our experimental measurements of k we initially tried to correct for interactions between gas and water molecules in the vapor phase by calculating the virial cross-term B_{ij} , using methods discussed in Hirschfelder et al. (1967). The results were not adequate for the high precision of the measurements, and we finally adopted the empirical approach.

In Fig. 1 we illustrate the significance of these corrections and compare the experimental values for C^*_0 from Montgomery et al., Carpenter, and Murray and Riley with those calculated from Eq. 21 using our values of k_0 . [The results from Klotz and Benson (1963a) are not included here because we want to focus on the directly measured C^*_0 values. Benson et al. (1979) showed that the results of Klotz and Benson, Carpenter, and Montgomery et al. are quite similar.] The reference line in Fig. 1 is based on our smooth values for k_0 , and the tight fit of the solid circles to it indicates the high precision of the measurements. Before plotting the percentage deviations of the experimental values for C^*_0 from the three sources, we expressed their values in $\mu\text{g-atoms}\cdot\text{dm}^{-3}$ as follows. Montgomery et al. expressed their results as the number of milligrams of dissolved oxygen per liter of solution, with the volume determined at 20°C rather than at the temperature of equilibrium. We have used

$$C^*_0 = C^{\text{me}} \times \frac{2 \times 10^3}{31.9988} \times \frac{\rho}{\rho_{20}},$$

where ρ and ρ_{20} are the densities of water at the equilibrium temperature and 20°C, to obtain the corresponding values for C^*_0 . Only values from Carpenter's table 1 have been included here, and they have been multiplied by his conversion

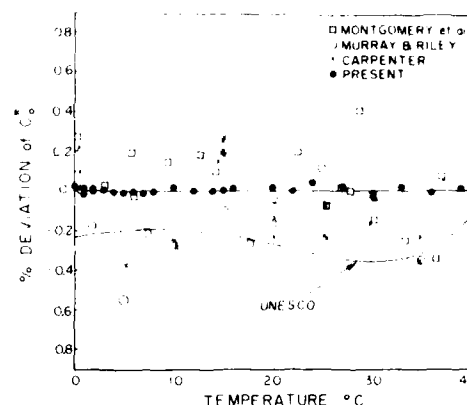


Fig. 1. Percentage deviations from our present smoothed values for C^*_0 in $\mu\text{g-atoms}\cdot\text{dm}^{-3}$ of the measured values from Montgomery et al., Carpenter, and Murray and Riley, and of the UNESCO smoothed values. Dashed lines indicate possible range of uncertainty of our present smoothed values.

factor $89.28 \mu\text{g-atoms}\cdot\text{ml}^{-1}$. Murray and Riley stated that they used a modification of the method of Carpenter (1965), in which the factor 5,598 ml of O_2 per equivalent is given. Accordingly, we have multiplied the Murray and Riley experimental values (by the Winkler method only) by $89.318 \mu\text{g-atoms}\cdot\text{ml}^{-1}$.

The dashed lines in Fig. 1 indicate the range of possible virial corrections for oxygen. If no correction were made, i.e. if the factor $(1 - \theta_0)$ in Eq. 21 were taken to be unity, the reference line and the solid circles would move upward (relative to the other three sets of results) to the position of the upper dashed line. The shift would vary from about 0.1% at

Table 3. Comparison of deviations of experimental values for C^*_0 from our present results.

Source	$\frac{\sum \% \text{ dev.}}{n}$	$\left[\frac{\sum (\% \text{ dev.})^2}{n} \right]^{1/2}$
Murray and Riley 1969	-0.15	0.25
Carpenter 1966	-0.05	0.22
Montgomery et al. 1964	+0.02	0.20
Present	0	0.017

0°C to 0.05% at 40°C. On the other hand, if we assumed that the correction for the air-water system were the same as the empirical correction found by Benson et al. (1979) for the pure oxygen-water system, then $(1 - \theta_0)$ would be replaced by $[1 - (\lambda_0 - \theta_0)]$, where λ_0 is given by Benson et al. as a function of temperature. With this assumption the reference line would become the lower dashed line, which is about 0.085% lower at 0°C and 0.03% lower at 40°C.

In principle, comparison of the results from the two kinds of measurements could test the possibilities discussed above, but it is clear from Fig. 1 that the scatter in the three sets of previous data is too large. A precision of about 0.02% for the direct C^*_0 measurements would be required for such a test. Nevertheless, within their random errors the older data are in general agreement with our results. The Montgomery et al. and Carpenter values are distributed approximately equally above and below the reference line, while the Murray and Riley points tend to be slightly lower. These comparisons are expressed in another way in Table 3, which shows that the Montgomery et al. and Carpenter deviations each average essentially to zero with an rms deviation of about 0.2%, and the Murray and Riley deviations average 0.15% low with an rms deviation of 0.25%. Table 3 differs somewhat from Table 3 in Benson et al., primarily because there the $[1 - (\lambda_0 - \theta_0)]$ correction was applied to the three sets of experimental C^*_0 values, and a different conversion factor was used for the Murray and Riley values.

Although we cannot determine the best correction to choose for calculating C^*_0 from values for k_0 , the two dashed lines in Fig. 1 provide probable limits of uncertainty and permit an estimation of the accuracy of the values in Table 1. Because the second virial coefficient for nitrogen is smaller than that for oxygen, the $[1 - (\lambda_0 - \theta_0)]$ correction probably is too large. On the other side, it is improbable that no virial correction would be required. Including the possible 0.02% systematic error in k_0 given by Benson et al.,

we estimate roughly that the values of C^*_0 and C^\dagger_0 in Table 1 are good to better than $\pm 0.07\%$ at lower temperatures and perhaps $\pm 0.04\%$ near 40°C. These uncertainties are negligible for studies of natural waters.

Weiss (1970) fitted the Carpenter (1966) and Murray and Riley (1969) data for both freshwater and seawater to four-term Valentiner-type functions for the variation of C^*_0 and C^\dagger_0 with temperature, with an additional three terms for the dependence on salinity. His values lie below our results by only 0.05–0.10% at low temperatures. Although they deviate more significantly above 20°C, the values of Weiss still agree with ours within the uncertainties of the previous data.

In 1976, Postma et al. constructed the UNESCO *International Oceanographic Tables* from the equations of Weiss. Unfortunately, they apparently assumed that the values of Weiss were given as the volume the gas would occupy at STP if it were *ideal*. (The factor 89.23 used by Postma et al. to convert from volume of gas at STP to $\mu\text{g-atoms}$ is equivalent to $22,414 \text{ cm}^3 \cdot \text{mol}^{-1}$.) In fact, Weiss (pers. comm.) intended his values to be expressed in terms of the volume which would be occupied by a *real* gas at STP. (The corresponding conversion factor would be 89.318, which is equivalent to $22,392 \text{ cm}^3 \cdot \text{mol}^{-1}$.) The UNESCO values are systematically low by from 0.15 to 0.35%. This is shown in Fig. 1, which includes a plot of the deviations of the UNESCO values from ours.

It should be noted that it is equally proper to express the amount of dissolved gas in terms of its STP volume as a real gas or as a hypothetical ideal gas, *provided* that it is made clear which is being used. We prefer the ideal gas notation, because the values specified do not depend on the state of our knowledge of the virial coefficients of the gas. The best procedure, however, is to eliminate the source of confusion by expressing the amount of dissolved gas directly in $\mu\text{g-atoms}$ (or μmol) or mg. Other reasons for this choice are discussed by Helland-Hansen et al. (1948) and Carpenter (1966). We have included the volume

specification in our equations and tables only because of its historical use.

We pointed out earlier that the Henry coefficient k is the quantity most fundamental to describing the solution process. On the other hand, for many geochemical and engineering purposes C^* (or C^\dagger) is the directly applicable quantity. To obtain the Bunsen coefficient from either k or C^* requires assumptions about the behavior of the vapor phase. Furthermore, because of molecular interactions in the vapor phase, the Bunsen coefficient is not a constant at a given temperature, but is a function of the total pressure (Eq. 15). This means that for precise work the Bunsen coefficient loses its primary usefulness, because we cannot simply multiply it by the partial pressure of the gas above a solution to obtain the equilibrium concentration of the gas in the solution. In general, it is necessary to use Eq. 11 to calculate C or, when the gas mixture is air, C^* , C^\dagger , or C^p can be used as discussed above. For these reasons, we suggest that in describing the solubility of a gas, emphasis should be placed on k , C^* , or C^\dagger rather than on the Bunsen coefficient. Avoiding the latter would have the additional advantages of eliminating the confusion associated with the many different ways it has been defined and of settling the conflict over whether to use the symbol α for the Bunsen coefficient or for the isotopic fractionation factor. We agree with the suggestion by Weiss (1970) that α be used for the latter.

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